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Double Dehydro-Diels–Alder Reactions of 1,5-Dien-3-ynes

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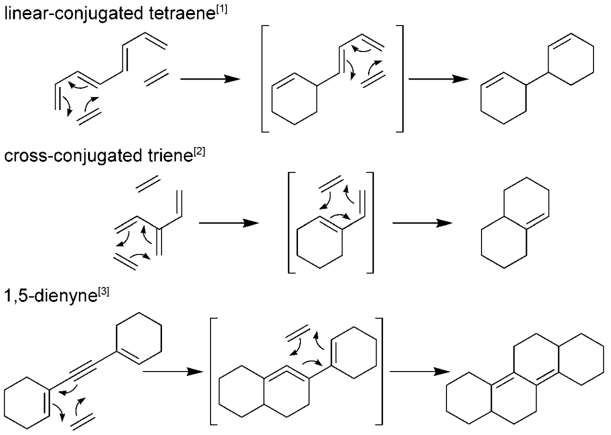
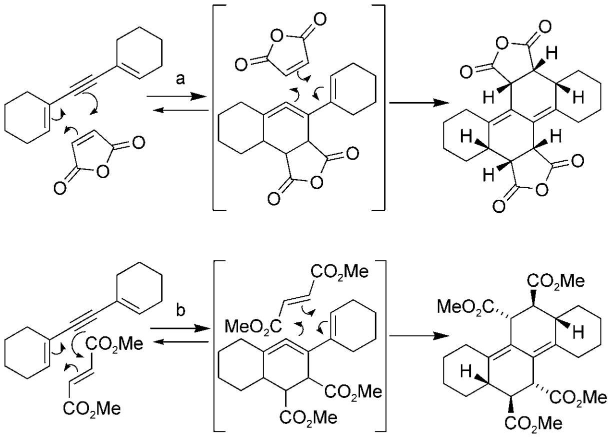
Double Diels–Alder reactions of conjugated bis-dienes are a group of very powerful processes that allow the generation of four covalent bonds in a "one-pot" process.[1–3] Three structurally distinct conjugated bis-dienes can be envisaged (Scheme 1): linear-conjugated tetraenes, in which two 1,3-butadienes react independently;[1] cross-conjugated trienes, in which the first cycloaddition generates a new diene for reaction in the second cycloaddition (a diene-transmissive Diels–Alder sequence);[2] and 1,5-dien-3-ynes, where the two central carbons participate in both cycloadditions (a double dehydro-Diels–Alder reaction).[3]



Scheme 1. Three variants of the double Diels–Alder reaction.

By far the least well studied of these is the reaction of 1,5-dien-3-ynes. This transformation was first reported in 1933 by Blomquist and Marvel.[3a] A series of reports by Butz and co-workers followed, in which the scope of the reaction was examined.[3b–h] Consistently low yields (2–19%) were reported for this rare[4] transformation. The stereochemistry of the products was not reported at that time, though a cyclic allene intermediate was proposed. This reaction has since remained largely uninvestigated; the exceptions being a report in 1952 by Ray and co-workers[3i,5] and another in 1996 by Miller and co-workers.[3j] In the latter paper, Miller and co-workers[3j] re-examined the reactions of dicyclohexenyl acetylene with maleic anhydride and dimethyl fumarate (Scheme 2). The authors report a single stereoisomeric product in each case (compounds **12** and **21** of this paper), as confirmed by single-crystal X-ray structure analy-



Scheme 2. Double dehydro-Diels–Alder reactions of 1,5-dien-3-ynes reported by Butz and co-workers (a and b)[5d,f] and stereochemistry reported by Miller and co-workers.[3j] Reagents and conditions: a) CO_2, 150 °C, 19%; b) N_2, 175 °C, 24 h, 15%.

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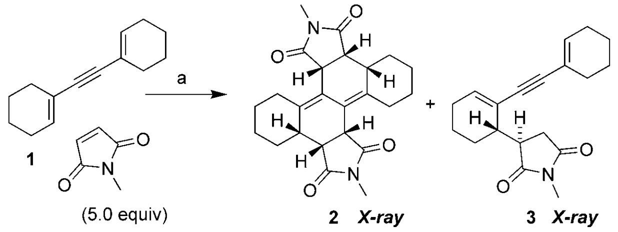
sis. The authors concluded that the reaction proceeds through two concerted cycloadditions, the first of which was proposed to be reversible. The *syn* adduct was reported as the exclusive product in both cases, a result which was erroneously attributed to a second dienophile addition to the "outside" face of the "cup-shaped" monoadduct. (The *syn*-bisadduct must arise from both dienophiles approaching from the same face of the dienyne.) In this report, neither reaction conditions nor yields were disclosed.

The rather obvious synthetic potential of this transformation coupled with its neglected status—in both an experimental and theoretical sense—led us to initiate a research programme in this area to further investigate this intriguing reaction. At the outset, it was our intention to: a) improve upon the very low yields in all previous reports of this transformation; b) examine the stereoselectivity of the reaction; c) investigate the scope and limitations of the process; d) develop an understanding of both the mechanism and the stereoselectivity of the reaction, by way of high level computational analysis.

Upon analysis of prior art,[3] some general features of this unique double Diels–Alder reaction are evident: it proceeds only at high temperature; the dienophile must be highly activated and yields are always low. *N*-Methylmaleimide (NMM) and 1,2-dicyclohexenyl acetylene **1** were chosen as representative reaction partners for our optimisation study. During the course of these investigations the following parameters were varied: a) temperature (110–190 °C); b) method of heating (conventional versus microwave); c) reaction time (5 min–45 h); and d) reaction stoichiometry (2.2–10.0 equiv of dienophile). We also explored the effects of various radical inhibitors, solvents and treated glassware. Initially, and consistent with literature reports,[3] we obtained poor isolated yields of products (11–22 %). After much experimentation, we were delighted to find that under optimised reaction conditions (Scheme 3) the double dehydro-Diels–Alder adduct **2** was obtained in a much improved 61 % yield along with ene product **3** in a 4 % yield. The structure and stereochemistry of both products were confirmed by single-crystal X-ray analysis.[6] Notably, *only one stereoisomer of both products could be detected.* Lowering the reaction temperature failed to improve the yield of the bisadduct and below about 130 °C, the solvent-free transformation required prohibitively long reaction times. The use of toluene and xylene as solvents did not lead to improved yields and again, prompted much longer reaction times.



Scheme 3. Double dehydro-Diels–Alder reaction of 1,2-dicyclohexenyl acetylene (**1**) with NMM. Reagents and conditions: a) dienyne **1** (1.0 equiv), NMM (5.0 equiv), hydroquinone (0.1 equiv), μwave, 300 W, 190 °C, 30 min, **2**: 61 %, **3**: 4 %.

Under these optimised conditions only about 67 % of the dienyne was accounted for in the isolated products and recovered dienyne; a complex mixture of polar degradation products made up the mass balance. The bisadduct was shown to survive the reaction conditions with little degradation. Re-subjecting ene product **3** to standard reaction conditions, however, afforded only polar degradation products. These results lead us to suspect that the ene reaction is a significant competing pathway to that leading to the double dehydro-Diels–Alder product, and the polar products making up the mass balance from the reaction depicted in Scheme 3 result from the ene product.

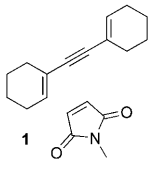
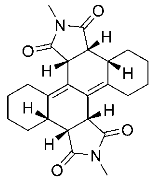
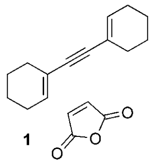
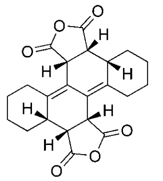
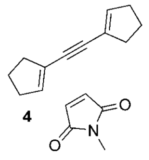
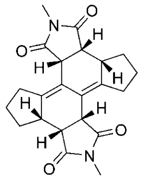
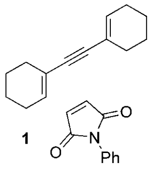
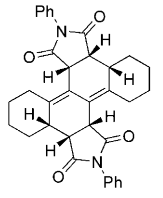
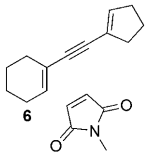
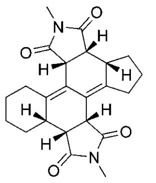
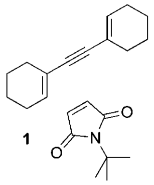
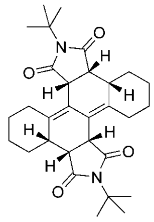
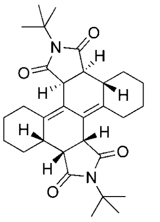
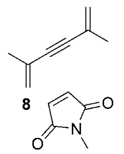
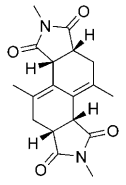
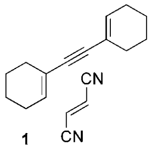
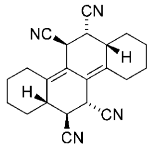
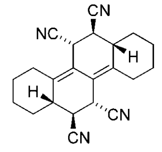
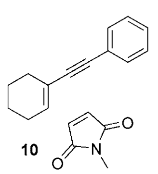
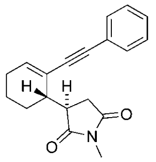
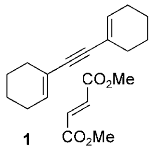
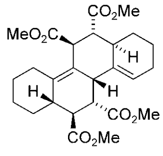
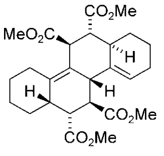
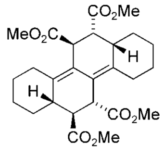
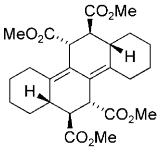
Keeping with NMM as dienophile, the optimised reaction conditions were applied to a range of 1,5-dien-3-ynes (Table 1, entries a–d). In each case, only the *endo,endo,syn*-isomer of the bisadducts was observed, as confirmed by single-crystal X-ray structure analyses.[6] The yields of the double Diels–Alder products were in the 40–60 % range. Interestingly, the reaction of 2,5-dimethylhexa-1,5-dien-3-yne **8** (Table 1, entry d) was considerably slower than the 'semicyclic' dienynes **1**, **4** and **6** (Table 1, entries a, b and c). Phenyl acetylenes have been successfully used in *single* (intramolecular)[4] dehydro-Diels–Alder reactions reported by Baddar and co-workers,[7] Saá and co-workers,[8] and others.[9] Interestingly, phenyl enyne **10** (Table 1, entry e) did not furnish the desired double dehydro-Diels–Alder product, but instead the major product **11** was that derived from the ene pathway.[10]

Next, the scope of the reaction with respect to the dienophile was examined (Table 1, entries f–j). Both *Z* and *E* electron poor dienophiles participate in the reaction, with isolated yields in the 36–61 % range. Whilst only the expected *endo,endo,syn*-bisadduct was observed in the reaction with maleic anhydride (Table 1, entry f) and *N*-phenylmaleimide (Table 1, entry g), *N*-*tert*-butylmaleimide afforded two diastereoisomeric bisadducts **14** and **15** in a ca. 2:1 ratio (Table 1, entry h). As elucidated by single-crystal X-ray structure analysis,[6] the major product was once again the *endo,endo,syn*-isomer **14**, but a new isomer, namely the *endo,exo,syn*-adduct **15**, was also formed.

The reactions with *E*-dienophiles were particularly interesting. Fumaronitrile afforded two stereoisomeric bisadducts **16** and **17** in a 72:28 ratio (Table 1, entry i).[11] In contrast, dimethyl fumarate gave four products (**18**–**21**) in a high overall yield (Table 1, entry j). This is at odds with previous reports.[12] The two minor products, **20** and **21**, are analogous to those obtained from the fumaronitrile reaction. The two major products **18** and **19**, however, are the result of an *anti*-double addition pathway followed by a formal 1,3-hydride shift.

These results prompt several questions relating to the mechanism and origin of stereoselectivity in the double dehydro-Diels–Alder sequence: 1) Do the two dienophiles add through concerted Diels–Alder processes? 2) What is the nature of the intermediate and is it formed reversibly?

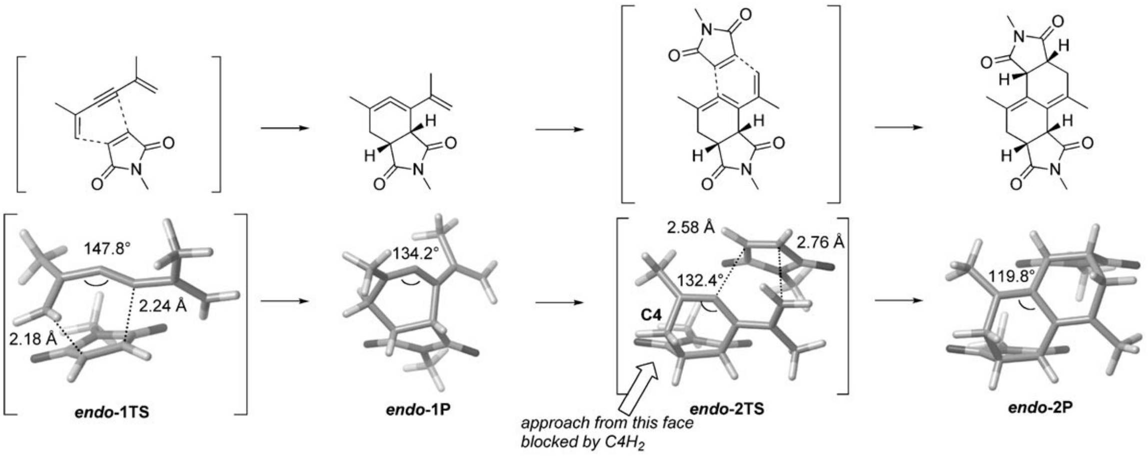
Table 1. Double dehydro-Diels–Alder reactions of a range of 1,5-dien-3-ynes and dienophiles.

Entry	Dienyne and dienophile	Product[a]	Yield [%][b]	Entry	Dienyne and dienophile	Product[a]	Yield [%][b]
a	 1	 2 *X-ray*	61	f[e]	 1	 12	36
b	 4	 5 *X-ray*	53	g	 1	 13 *X-ray*	50
c	 6	 7 *X-ray*	58	h[f]	 1	 *X-ray* 14 63:37  15 *X-ray*	36
d[c]	 8	 9 *X-ray*	37	i[e]	 1	 *X-ray* 16 72:28  17 *X-ray*	44
e	 10	 11	48[d]	j[g]	 1	 *X-ray* 18 44:42  19 *X-ray*  20 6:7  21 *X-ray*	81

[a] Reagents and conditions: dienyne (1.0 equiv), dienophile (5.0 equiv), hydroquinone (0.1 equiv), μwave, 300 W, 190 °C, 30 min. [b] Isolated yields. [c] Sealed tube, 130 °C, 12 h. [d] 25 % enyne recovered. [e] Reaction time of 1 h. [f] Reaction time of 2 h. [g] Without hydroquinone, sealed tube, 170 °C, 17 h.

3) What is the origin of the exclusive *syn*-π-diastereofacial selectivity witnessed in all but the dimethyl fumarate reaction? These questions were addressed through computational analysis of the reaction of NMM with 2,5-dimethylhexa-2,5-dien-3-yne **8** using density functional theory employing the M05-2X hybrid functional.[13]

Both NMM additions to the dienyne were found to be concerted processes and the 6-membered cyclic allene was calculated to be a stable structure. The *endo*-transition structures (TSs) of the first and second cycloaddition events are depicted in Scheme 4, along with the structures of the cyclic allene intermediate and double dehydro-Diels–Alder adduct. A non-concerted addition to the dienyne to form a biradical intermediate is considerably less favoured, with an activation enthalpy 31.5 kJ mol^{-1} higher than that for the concerted DA reaction. The activation enthalpy for the concerted *endo* mode of addition of NMM to the dienyne is predicted to be 67.6 kJ mol^{-1} (see the Supporting Information, Table S1), which is 25.5 kJ mol^{-1} higher than the value of 42.1 kJ mol^{-1} calculated for the reaction of NMM with



Scheme 4. Transition states of the two cycloadditions and the calculated structure of the allene intermediate.

1,3-butadiene. The *endo* TS is 20 kJ mol^{-1} lower in enthalpy than the *exo* TS, signifying that the first addition takes place exclusively by the *endo* path.[14] The *endo*-preference in the first addition event can be traced to destabilising steric strain between the spectator isopropenyl group and the NMM in the *exo*-TS; a destabilising interaction which is expected to be of higher magnitude in dienynes carrying bulkier substituents than methyl groups.

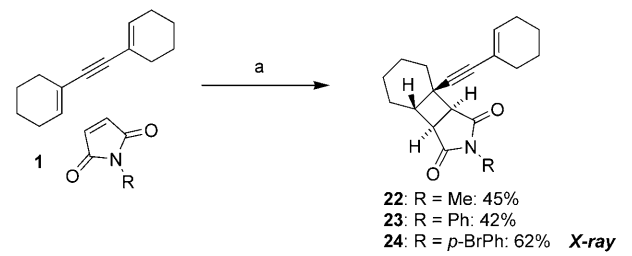
Interestingly, the first cycloaddition reaction is significantly exothermic, by 104 kJ mol^{-1} (see the Supporting Information, Table S1), notwithstanding the formation of the strained cyclohexa-1,2-diene ring (allene bond angle 134.2°). *This value precludes the possibility of a reversible first cycloaddition event under the reaction conditions.*[15]

Turning to the second Diels–Alder reaction between NMM and the 1-propenyl-cyclohexa-1,2-diene *endo*-monoadduct, two aspects of stereoselection need to be considered, namely *endo/exo* selectivity and π-diastereofacial selectivity. The cyclohexa-1,2-diene ring in the *endo*-monoadduct adopts a boat conformation, and this controls the direction of approach of NMM. As may be seen from Scheme 4, whereas approach from the face *syn* to the pre-existing imide ring is relatively free of steric interference, the C4H$_2$ group blocks approach by NMM from the *anti*-face. So far, attempts to locate TSs arising from NMM approach to the *anti*-face have failed. The *endo,syn*-TS for the second addition is strongly favoured over the corresponding ***exo*-2TS** by 26.4 kJ mol^{-1} and leads to the formation of the observed *endo,endo,syn* bisadduct. Since no obvious destabilising interactions can be identified in the ***exo*-2TS**, we presume that the *endo*-selectivity seen with NMM is the result of secondary orbital interactions at play in the ***endo*-2TS**. Experimentally, of the cyclic *Z*-dienophiles, only *N-tert*-butylmaleimide gives a product other than the *endo,endo,syn*-isomer (Table 1, entry h). In this case, unfavourable steric interactions between the two imide moieties destabilise ***endo*-2TS**, allowing the corresponding ***exo*-2TS** to compete, thus leading to a small amount of the *endo,exo,syn*-isomer. Interestingly, ***endo*-2TS** lies enthalpically 27.2 kJ mol^{-1} *below* the monoadduct plus free NMM (see the Supporting Information, Table S1). Intrinsic reaction coordinate analysis on the ***endo*-2TS** led to a pre-**2TS** complex, lying 1.8 kJ mol^{-1} lower in energy at 0 K but is essentially isoenthalpic with the ***endo*-2TS** at 298 K. The free energy of activation for the second addition is only 17.8 kJ mol^{-1} (relative to the pre-**2TS** complex) which is consistent with the very high general reactivity observed for cyclohexa-1,2-dienes.

While a full explanation of the stereoselectivities witnessed with the *E*-dienophiles requires further study, we presume that these reactions also proceed through concerted double Diels–Alder pathways, akin to that depicted in Scheme 4. In the case of the fumaronitrile reaction (Table 1, entry i), the two observed products are the result of *syn*-addition of the two dienophiles to the dienyne, whereas with dimethyl fumarate (Table 1, entry j), the two major products are the result of an *anti*-addition pathway. For both reactions, three *syn*-diastereomers and three *anti*-diastereomers are possible so again, these double Diels–Alder reactions are exhibiting significant levels of stereoselection. Evidently, with *E*-dienophiles both *endo/exo*- and π-diastereofacial selectivities are controlled by subtle factors.

The discovery of Lewis acid promotion[16] is one of the most significant contributions to Diels–Alder chemistry, greatly enhancing the scope of the reaction and leading to unprecedented control of chemo-, regio- and stereoselectivities. Encouraged by the successful application of Lewis acids in *single, intramolecular* dehydro-Diels–Alder reactions,[9,17] we anticipated a productive outcome with these *double, intermolecular* dehydro-Diels–Alder processes. To our surprise, however, when dienyne **1** was treated with a 1:1 complex of MeAlCl$_2$ and maleimide-based dienophiles, in each case a single diastereomer of the [2+2] adduct was obtained in 40–60 % isolated yield (Scheme 5). To our knowledge, these are the first examples of a Lewis acid promoted [2+2] cycloaddition reactions of an enyne.[18]

In conclusion, polycyclic ring systems can be formed in synthetically useful yields by the double dehydro-Diels–Alder reactions of readily available 1,5-dien-3-ynes and al-



22: R = Me: 45%
23: R = Ph: 42%
24: R = *p*-BrPh: 62%

Scheme 5. Lewis acid-promoted reactions of dienyne **1**. Reagents and conditions: a) maleimide (4.6 equiv), $MeAlCl_2$ (4.5 equiv), toluene, −78 °C to room temperature, 1.5 h.

kenic dienophiles. The transformation involves the formation of two new rings, six stereocentres and four C–C bonds. With *Z*-dienophiles, a strong preference for the *endo,endo,-syn*-isomer is witnessed. Computational studies support a mechanism involving two concerted cycloaddition events and a 1,2-cyclohexadiene intermediate. It is fair to say that the relatively narrow scope of this process currently limits its applicability in synthesis. Nevertheless, we believe that these new insights will serve as a platform for the further development of this unique and very powerful transformation.

Experimental Section

Typical procedure: To a microwave vessel equipped with a magnetic stirrer bar was added the dienyne (0.5 mmol, 1 equiv), dienophile (2.5 mmol, 5 equiv) and hydroquinone (0.05 mmol, 0.1 equiv). The vessel was purged with a stream of nitrogen and capped before being heated in a microwave reactor. After cooling, the crude product(s) were isolated by flash chromatography on silica.[19]

Acknowledgements

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Keywords: cycloaddition · density functional calculations · domino reactions · stereoselectivity · strained compounds

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[1] For double Diels–Alder reactions of linear conjugated tetraenes see: a) G. A. Kraus, M. J. Taschner, *J. Am. Chem. Soc.* **1980**, *102*, 1974; b) M. Nörret, M. S. Sherburn, *Angew. Chem.* **2001**, *113*, 4198; *Angew. Chem. Int. Ed.* **2001**, *40*, 4074; c) C. I. Turner, R. M. Williamson, P. Turner, M. S. Sherburn, *Chem. Commun.* **2003**, 1610; d) C. I. Turner, M. N. Paddon-Row, A. C. Willis, M. S. Sherburn, *J. Org. Chem.* **2005**, *70*, 1154.

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[6] See the Supporting Information for details. CCDC-743124, CCDC-743125, CCDC-743126, CCDC-743127, CCDC-743128, CCDC-743129, CCDC-743130, CCDC-743131, CCDC-743132, CCDC-743133, CCDC-743134, CCDC-743135, CCDC-743136 and CCDC-743137 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] a) F. G. Baddar, L. S. El-Assal, *J. Chem. Soc.* **1948**, 1267; b) F. G. Baddar, L. S. El-Assal, *J. Chem. Soc.* **1951**, 1844; c) F. G. Baddar, H. A. Fahim, M. A. Galaby, *J. Chem. Soc.* **1955**, 465; d) F. G. Baddar, L. S. El-Assal, N. A. Doss, *J. Chem. Soc.* **1959**, 1027; e) F. G. Baddar, G. E. M. Moussa, M. T. Omar, *J. Chem. Soc. C* **1968**, 110.

[8] a) D. Rodríguez, A. Navarro, L. Castedo, D. Domínguez, C. Saá, *Org. Lett.* **2000**, *2*, 1497; b) D. Rodríguez, A. Navarro-Vázquez, L. Castedo, D. Domínguez, C. Saá, *J. Org. Chem.* **2003**, *68*, 1938; c) D. Rodríguez, A. Navarro-Vázquez, L. Castedo, D. Domínguez, C. Saá, *J. Am. Chem. Soc.* **2001**, *123*, 9178.

[9] For a recent review see: P. Wessig, G. Müller, *Chem. Rev.* **2008**, *108*, 2051.

[10] The stereochemistry of **11** was assigned by analogy with **3**. See the Supporting Information for more details.

[11] For the bisadducts formed from fumaronitrile and dimethyl fumarate, the terms *endo* and *exo* are imprecise.

[12] Minor adduct **21** had previously been reported as the sole product from the reaction of dicyclohexenyl acetylene and dimethyl fumarate. See reference [3j] for more details.

[13] The M05–2X hybrid functional was used because of its demonstrated ability to give balanced and reliable thermochemical kinetics data (Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory Comput.* **2006**, *2*, 364). Geometries of reactants, products and transition structures (TSs) were optimised by using the 6-31G(d) basis set and more reliable enthalpies and free energies of all stationary points were obtained from single-point energy calculations using the 6-311++G(2df,p) basis set (M05–2X/6–311++G(2df,p)//M05–2X/6-31G(d)) in conjunction with M05–2X/6-31G(d)ZPE and thermal corrections ($T=298.15$ K).

[14] The experimental result for the double dehydro-Diels–Alder addition of NMM to 2,5-dimethyl-1,5-dien-3-yne **8** sheds no light on the *endo*/*exo* selectivity of the first Diels–Alder addition.

[15] The computed reaction enthalpy for the Diels–Alder reaction between NMM and 1,3-butadiene is -181 kJ mol^{-1}.

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[17] a) R. L. Danheiser, A. E. Gould, R. F. de la Pradilla, A. L. Helgason, *J. Org. Chem.* **1994**, *59*, 5514; b) J. R. Dunetz, R. L. Danheiser, *J. Am. Chem. Soc.* **2005**, *127*, 5776; c) H. M. R. Hoffmann, D. Krumwiede, H. H. Oehlerking, G. W. Prahst, *Tetrahedron* **1993**, *49*, 8999.

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[19] See the Supporting Information for more details.

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