Diels–Alder reactions of 1,1,3-triarylallyl cations: determination of the free energy of concert †‡

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1,1,3-Triarylallyl cations react with 1,3-dienes to give Diels–Alder products in low to moderate yields. The observed second-order rate constants agree with those calculated for the stepwise processes by the correlation $\log k(20\ °C) = s(N + E)$ [eqn. (1)] indicating the absence of a significant free energy of concert. Eqn. (1) can, therefore, also be employed for the prediction of absolute rate constants of Diels–Alder reactions of allyl cations.

Introduction

The acceleration of [4+2]-cycloadditions by acceptor groups in the dienophile (Scheme 1) has long been known and is
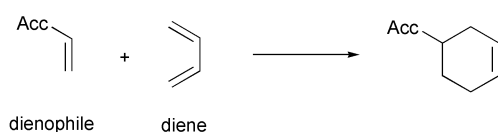
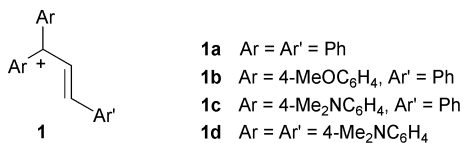**Scheme 1** Diels–Alder reaction of an acceptor-substituted dienophile with a diene.

usually referred to as the "Alder rule".[1] PMO theory rationalises this phenomenon by the lowering of the LUMO of the dienophile and the reduction of the energy difference between HOMO (diene) and LUMO (dienophile).[2] Relative reactivities of dienophiles have been explained in this way.[3]

Recently we have demonstrated that the rates of the reactions of carbocations with nucleophiles are given by the three-parameter eqn. (1),[4–6]

$$\log k(20\ °C) = s(N + E) \tag{1}$$

where s = nucleophile-specific slope parameter, N = nucleophilicity parameter and E = electrophilicity parameter.

Since the allyl cations **1** can be considered as acceptor substituted dienophiles,[7–9] they represent a class of compounds where kinetic aspects of Diels–Alder reactions can be investigated by the use of the correlation eqn. (1).

1a	Ar = Ar' = Ph
1b	Ar = 4-MeOC$_6$H$_4$, Ar' = Ph
1c	Ar = 4-Me$_2$NC$_6$H$_4$, Ar' = Ph
1d	Ar = Ar' = 4-Me$_2$NC$_6$H$_4$

For our analysis, the following line of arguments is used: if the cycloaddition of **1** with the 1,3-dienes **2** proceeds stepwise,

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† Dedicated to Professor W. Beck on the occasion of his 70th birthday.
‡ Electronic supplementary information (ESI) available: rate constants and experimental conditions of the individual kinetic experiments. See http://www.rsc.org/suppdata/p2/b2/b203555c/
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with rate-determining formation of **3a/b**, the observed reaction rate should be predictable by eqn. (1), since in this case electrophile and nucleophile combine with the formation of one new σ-bond, like the reactions of carbocations with olefins for which eqn. (1) was derived.[4,5] The cycloaddition will only proceed by a concerted mechanism if this reaction mode is energetically more favourable than the stepwise mechanism. The ratio between observed rate constant and rate constant for the hypothetical stepwise reaction calculated by eqn. (1) thus provides a measure for the "free energy of concert"[10] (Scheme 2). For calculating the rate of formation of **3a/b**, the
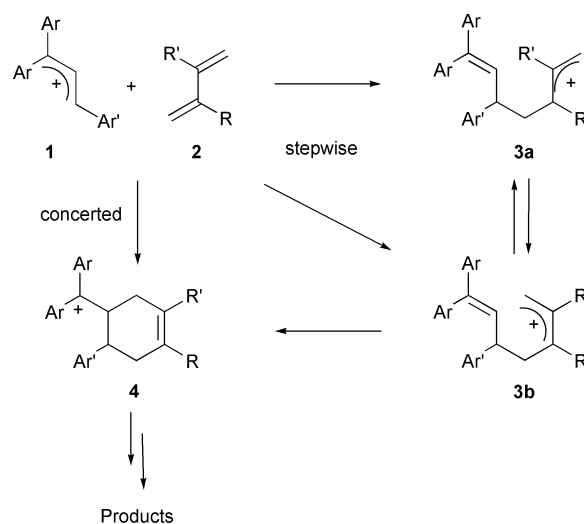
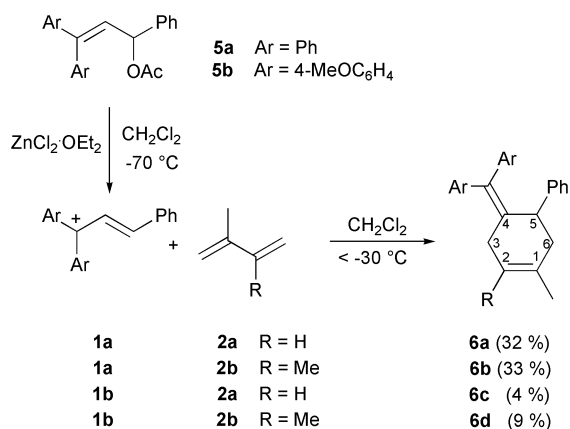**Scheme 2** Stepwise and concerted pathways of the Diels–Alder reactions of allyl cations **1** with dienes **2**.

previously published N and s parameters of the 1,3-dienes **2** and the E parameters of the allyl cations **1a–d** derived in the preceding article[11] can be used.

Results

Cycloaddition products

Combination of 1,3,3-triphenylprop-2-enyl acetate **5a** with ZnCl$_2$·OEt$_2$ at −70 °C in dichloromethane gave a dark-red solution of **1a** which reacted with isoprene (**2a**) and 2,3-

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Scheme 3

dimethylbuta-1,3-diene (**2b**) at −30 °C to afford the cyclohexene derivatives **6a** and **6b**, respectively (Scheme 3). Attempts to trap the intermediate cations **4** by addition of 2 equiv. of triethylamine–borane before aqueous work-up failed. It must, therefore, be concluded that deprotonation of the carbocations **4** to give **6a** and **6b** occurs under the conditions of the cyclo-additions and not during aqueous work-up.

The analogous reactions of 3,3-dianisyl-1-phenylprop-2-enyl acetate **5b** with **2a** and **2b** were very slow, and the cyclohexenes **6c,d** were obtained in low yields after five days at −45 °C (Scheme 3). Raising of the temperature was not attempted because of the well-known tendency of the intermediate allyl cations **1a,b** to undergo electrocyclic ring-closure with formation of indanyl cations.[12,13] The 4-methylene-5-phenylcyclohex-1-ene structure of compounds **6a–d** was recognised in the ^{1}H NMR spectra by the broad doublet absorption of the benzylic proton 5-H (δ 4.05–4.12) and the multiplets at δ 2.42–2.80 due to four allylic hydrogens (3-H$_2$, 6-H$_2$). Additional evidence comes from the ^{13}C NMR spectra of **6a–d** with three sp^3 and three sp^2 carbon resonances for the cyclohexene ring.

The low reactivity of the methyl substituted butadienes **2a,b** towards **1b** suggested that there would not be any chance to observe a reaction with the considerably less electrophilic[11] allyl cations **1c,d**. Actually, we have not even been able to isolate a product from **1c** and the more nucleophilic 2-(trimethyl-siloxy)buta-1,3-diene ($N = 4.83$, $s = 0.90$),[14] but the reactions of **1c,d**–BF$_4$ with Danishefsky's diene **2c** ($N = 8.57$, $s = 0.84$)[4] gave low to moderate yields of the cyclohexenones **7a** (51%) and **7b** (8%) (Scheme 4).
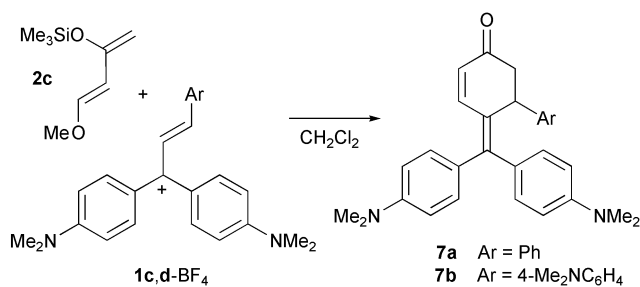
Scheme 4

Kinetics

When the purple solution of **1a**, generated in dichloromethane from **5a** and ZnCl$_2$·OEt$_2$, was treated with **2a** or **2b**, the colour disappeared, and the decay of the absorbance of **1a** at 510 nm was followed photometrically using the work-station described previously.[15] Since the dienes **2a,b** were used in large excess over **1a**, their concentrations remained almost constant during the reactions, and the pseudo-first-order rate constants k_{obs} could be divided by the concentration of the dienes to yield the second-order rate constants given in Tables S1–S3 of the

Supplementary Information. Because of the cyclisation[12,13] of **1a** above −30 °C, all kinetic experiments were performed between −70 and −50 °C. The $k(20 °C)$ values given in Table 1 were then extrapolated from the activation parameters determined in the low temperature range.

The slightly higher reactivity of **2b** over **2a** shown in Table 1 is comparable to the relative reactivities of these two dienes towards the 4-methoxy substituted benzhydryl cation ($k_{2b}/k_{2a} = 1.8$, −70 °C)[16] as well as towards the dienophiles maleic anhydride ($k_{2b}/k_{2a} = 2.2$, 30 °C)[17] and tetracyanoethylene ($k_{2b}/k_{2a} = 32$, 20 °C). The activation entropies given in Table 1 closely resemble those determined for the reactions of the dienes **2a,b** and other terminal olefins with benzhydryl cations[16] as well as those of concerted Diels–Alder reactions of non-charged cycloaddends,[3] indicating that $\Delta S^{\ddagger}$ is not a reliable criterion to differentiate between concerted and stepwise mechanisms.

Rate constants for the reactions of **1b** with **2a,b** could not be determined. When **1b** was treated with 100 equiv. of **2b** ($c = 35$ mmol l^{-1}) at −50 °C (CH$_2$Cl$_2$) no change of the intensity of the absorbance of **1b** could be detected within one day.

Because of the lower tendency of **1c** and **1d** to undergo cyclisation, their reactions with Danishefsky's diene **2c** could be investigated at 20 °C. Decolourisation of the green solution of **1c** and the blue solution of **1d** was followed photometrically at 675 nm and 600 nm, respectively, under pseudo-first-order conditions using the work-station described previously.[15,18] The second-order rate constants shown in Table 1 were obtained by averaging the results of several of kinetic experiments, which are documented in the Supplementary Information.

Discussion

The eventual formation of the cations **3a,b** from the dienophiles **1** and the dienes **2** closely resembles the electrophilic additions of benzhydryl cations to these dienes. For that reason, the rate constants $k_{calc}(20 °C)$ for the one-bond attack of the allyl cations **1a–d** at the dienes **2a–c** to give **3** can be calculated by eqn. (1). One can recognise that the calculated rate constants listed in the last column of Table 1 agree with the experimentally obtained values within a factor of 3, *i.e.*, the deviation is comparable to the standard deviation for predictions by eqn. (1) for reactions of these dienes with electrophiles other than benzhydryl cations.[4] It is, therefore, suggested that compounds **6** and **7**, consecutive products of the cations **4**, are produced by stepwise processes *via* intermediates **3a,b** or analogous allyl cations. Possibly, these intermediates can also undergo alternative consecutive reactions and thus account for the low yields of products isolated in some cases. Competing stepwise and concerted cycloadditions of the allyl cations **1a–d** with the dienes **2a–c** are also in accord with the experimental findings.

The close similarity of k_{calc} and k_{exp} rules out transition states, however, that are considerably stabilised due to the simultaneous formation of two new σ-bonds.[19] The reactions definitely do not have a high degree of concertedness. Theoretical investigations of the Diels–Alder reaction of the parent allyl cation with buta-1,3-diene came to the same conclusion.[20]

The failure to observe allyl cation diene combinations with $k_{calc} < 10^{-4}$ l mol^{-1} s^{-1} has an interesting consequence: obviously, a concerted mechanism cannot be turned on when the stepwise process becomes energetically unfavourable. For that reason, eqn. (1) can be used not only for the prediction of absolute rate constants for reactions of the allyl cations **1** with one-bond nucleophiles but also for predicting rate constants of their Diels–Alder reactions with 1,3-dienes.

Experimental

General

NMR spectra were recorded with Bruker ARX 300, Varian VRX 400S, and Varian INOVA-400 spectrometers. ^{1}H NMR

Diene	N^a	s^a	Dienophile	E^b	$\Delta H^\ddagger$/kJ mol$^{-1 g}$	$\Delta S^\ddagger$/J mol^{-1} K$^{-1 g}$	k_{exp}(20 °C)/ 1 mol^{-1} s^{-1}	k_{calc}(20 °C)/ 1 mol^{-1} s$^{-1 c}$
Isoprene (**2a**)	1.10	0.98	**1a**	+0.98	26.40 ± 0.66	−124.7 ± 3.0	3.68 × 10$^{1 d}$	1.09 × 10^2
Isoprene (**2a**)	1.10	0.98	**1b**	−2.67	—	—	—	2.89 × 10^{-2}
2,3-Dimethylbutadiene (**2b**)	1.17^e	1.00^e	**1a**	+0.98	28.26 ± 1.04	−105.2 ± 4.8	1.79 × 10$^{2 d}$	1.41 × 10^2
2,3-Dimethylbutadiene (**2b**)	1.17^e	1.00^e	**1b**	−2.67	—	—	—^{f}	3.16 × 10^{-2}
Danishefsky's diene (**2c**)	8.57	0.84	**1c**	−8.97	—	—	3.72 × 10^{-1}	4.61 × 10^{-1}
Danishefsky's diene (**2c**)	8.57	0.84	**1d**	−9.84	—	—	8.32 × 10^{-2}	8.57 × 10^{-2}

^{a} Nucleophilicity parameters N and s from ref. 4. ^{b} E parameters from ref. 11. ^{c} Calculated from eqn. (1) for the formation of **3a/b**. ^{d} Extrapolated from experiments at −70 to −50 °C. ^{e} From rate constant in ref. 16 using the parametrisation described in ref. 4. ^{f} Using similar concentrations as for the experiments with **1a**, no change of absorbance was detectable within 22 h at −50 °C. ^{g} Since the standard deviations of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ do not include systematic errors, the actual uncertainties are greater than indicated in this column. For that reason the listed decimals are meaningless by themselves but are needed to reproduce the rate constants given.

chemical shifts refer to tetramethylsilane (δ_H 0.00) and ^{13}C NMR chemical shifts refer to the solvent as internal standard (CDCl$_3$: δ_C 77.0). Coupling constants J are given in Hz. Mass spectra (EI, 70 eV) were obtained with a Varian MAT 90 or MAT 95 instrument. Melting points (uncorrected) were determined with a Reichert Thermovar apparatus.

The UV–VIS photometer used for the kinetic studies of reactions of **1a** was a Schölly KGS III with band-pass filters by Corion[15] whereas reactions of cations **1c** and **1d** were followed with a J&M TIDAS DAD connected to quartz-insertion probes by Hellma.[18] The kinetic measurements and the data-evaluation were carried out as described previously.[15]

All reactions were performed with exclusion of moisture in an atmosphere of dry nitrogen in carefully dried Schlenk glassware. Dichloromethane was freshly distilled from CaH$_2$ before use.

The compounds **1a**–**d** and the precursors **5a,b** were generated as described before.[11] Dichloromethane solutions of the Lewis acid ZnCl$_2$·OEt$_2$ were prepared with a molar Et$_2$O–ZnCl$_2$ ratio of 1.12 to achieve the highest catalytic activity according to the literature.[21] Dienes **2a**–**c** are commercially available.

The kinetic measurements and the data-evaluation were carried out as described previously.[11,15,16]

4-(Diphenylmethylene)-1-methyl-5-phenylcyclohex-1-ene (6a)

A solution of **5a** (0.22 g, 0.67 mmol) in dichloromethane (10 ml) was cooled to −70 °C. Then a solution of ZnCl$_2$·OEt$_2$ in dichloromethane[21] (1.0 ml, $c = 1.20$ mol l^{-1}) was added and the mixture was stirred for 10 min during which time its colour turned purple. After the addition of diene **2a** (0.22 ml, 0.15 g, 2.2 mmol) the reaction mixture was stirred for 21 h at −30 °C. Then saturated aq. NaHCO$_3$ (10 ml) was added with stirring and the mixture was allowed to warm to ambient temperature. The aqueous phase was separated and extracted with dichloromethane (10 ml). The combined organic phases were dried over MgSO$_4$ and filtered, and the solvent was evaporated *in vacuo* to yield 268 mg of a colourless oil which consisted of a mixture of polymer and cyclic product **6a** (yield 32%, as calculated from the ^{1}H NMR). A small amount of purified **6a** could be obtained by several recrystallisations from acetonitrile in which the polymer is poorly soluble, mp 121–123 °C (Found C, 92.50; H, 7.40. C$_{26}$H$_{24}$ requires C, 92.81; H, 7.19); δ_H (CDCl$_3$, 300 MHz)^{22} 1.80 (3 H, s, CH$_3$), 2.45–2.78 (4 H, m, 3-H$_2$ and 6-H$_2$), 4.09 (1 H, br d, J 5.5, 5-H), 5.25 (1 H, br s, 2-H), 7.09–7.37 (15 H, m, ArH); δ_C (CDCl$_3$, 75.5 MHz)^{22} 23.34 (q, CH$_3$), 28.59 (t, C-3), 35.48 (t, C-6), 41.22 (d, C-5), 121.09 (d, C-2), 125.84, 126.34, 126.50, 126.90, 127.88, 128.08, 128.30, 129.53, 129.68 (9 d, Ar), 132.26, 136.02, 136.87, 142.42, 142.96, 143.98 (6 s).

4-(Diphenylmethylene)-1,2-dimethyl-5-phenylcyclohex-1-ene (6b)

Compound **5a** (0.28 g, 0.85 mmol), a dichloromethane solution of ZnCl$_2$·OEt$_2$[21] (1.00 ml, $c = 1.20$ mol l^{-1}), and **2b** (0.33 ml,

0.24 g, 2.9 mmol) were reacted as described above. Work-up gave a yellow oil which contained polymer and the cyclic product **6b** (yield 33%, as calculated from the ^{1}H NMR). A small amount of purified **6b** could be obtained by several recrystallisations from acetonitrile in which the polymer is poorly soluble, mp 128–130 °C (Found C, 92.30; H, 7.25. C$_{27}$H$_{26}$ requires C, 92.52; H, 7.48); δ_H (CDCl$_3$, 300 MHz) 1.49, 1.76 (2 × 3 H, 2 s, 2 × CH$_3$), 2.44–2.72 (4 H, m, 3-H$_2$ and 6-H$_2$), 4.05 (1 H, br d, J 5.4, 5-H), 7.10–7.36 (15 H, m, ArH); δ_C (CDCl$_3$, 75 MHz) 18.82, 18.92 (2 q, 2 × CH$_3$), 34.55, 36.94 (2 t, C-3 and C-6), 41.56 (d, C-5), 123.85, 125.63 (2 s, C-1 and C-2), 125.72, 126.29, 126.45, 126.93, 127.85, 128.03, 128.27, 129.60, 129.82 (9 d, Ar), 135.43, 137.73, 142.42, 143.04, 144.21 (5 s).

4-[Bis(4-methoxyphenyl)methylene]-1-methyl-5-phenylcyclohex-1-ene (6c)

A solution of **1b** was produced at −70 °C from **5b** (0.23 g, 0.59 mmol) and a dichloromethane solution of ZnCl$_2$·OEt$_2$[21] (0.40 ml, 0.77 mmol, $c = 1.914$ mol l^{-1}) in dichloromethane (10 ml) as described above. Then diene **2a** (0.14 g, 2.1 mmol) was added, and the reaction mixture was stirred for 5 d at −45 °C. Work-up as above gave the crude product which was further purified by chromatography on neutral alumina with *n*-hexane–diethyl ether (20 : 1) as eluent to yield 24.2 mg of a mixture of polymer and **6c** (yield 4%, as calculated from the ^{1}H NMR) as a pale yellow oil. δ_H (400 MHz, CDCl$_3$)^{22} 1.80 (3 H, s, CH$_3$), 2.46–2.80 (4 H, m, 3-H$_2$ and 6-H$_2$), 3.77, 3.80 (2 × 3 H, 2 s, 2 × OCH$_3$), 4.12 (1 H, br d, J 5.5, 5-H), 5.24 (1 H, br s, 2-H), 6.76–6.80, 6.85–6.89, 6.98–7.02 (3 × 2 H, 3 m, ArH), 7.12–7.26 (m, 7 H, ArH); δ_C (100 MHz, CDCl$_3$)^{22} 23.34 (q, CH$_3$), 28.76 (t, C-3), 35.45 (t, C-6), 41.25 (d, C-5), 55.16, 55.20 (2 q, 2 × OCH$_3$), 113.20, 113.67 (2 d, Ar), 121.24 (d, C-2), 125.76, 126.88, 128.03, 130.59, 130.85 (5 d, Ar), 132.20, 135.06, 135.24, 135.74, 135.96, 144.21, 158.01, 158.18 (8 s).

4-[Bis(4-methoxyphenyl)methylene]-1,2-dimethyl-5-phenylcyclohex-1-ene (6d)

Compound **5b** (0.22 g, 0.57 mmol), a dichloromethane solution of ZnCl$_2$·OEt$_2$[21] (0.40 ml, 0.77 mmol, $c = 1.914$ mol l^{-1}), and diene **2b** (0.15 g, 1.8 mmol) were allowed to react for 5 d at −45 °C as described above for the formation of **6c**. Work-up as above yielded a crude product which was purified by chromatography on neutral alumina with *n*-hexane–diethyl ether (20 : 1) as eluent to give 39.5 mg of a mixture of polymer and **6d** (yield 9%, as calculated from the ^{1}H NMR) as a pale yellow oil. δ_H (400 MHz, CDCl$_3$)^{22} 1.49, 1.75 (2 × 3 H, 2 s, 2 × CH$_3$), 2.42–2.66 (4 H, m, 3-H$_2$ and 6-H$_2$), 3.77, 3.79 (2 × 3 H, 2 s, 2 × OCH$_3$), 4.08 (1 H, br d, J 5.5, 5-H), 6.77–6.81, 6.84–6.89, 6.99–7.03 (3 × 2 H, 3 m, ArH), 7.12–7.23 (7 H, m, ArH); δ_C (100 MHz, CDCl$_3$)^{22} 18.82, 18.93 (2 q, 2 × CH$_3$), 34.73, 36.91 (2 t, C-3 and C-6), 41.57 (d, C-5), 55.13, 55.18 (2 q, 2 × OCH$_3$), 113.16, 113.63 (2 d, Ar), 123.78 (s, C-1 or C-2), 125.63 (d, Ar),

125.74 (s, C-1 or C-2), 126.90, 127.98, 130.64, 130.96 (4 d, Ar), 134.47, 135.24, 135.79, 136.81, 144.43, 157.94, 158.13 (7 s).

4-[Bis(4-dimethylaminophenyl)methylene]-5-phenylcyclohex-2-enone (7a)

A mixture of **1c**–BF$_4$ (0.43 g, 0.97 mmol) and diene **2c** (0.40 ml, 0.36 g, 2.1 mmol) in dichloromethane (10 ml) was stirred for 1 h at ambient temperature. After addition of 2 M NaOH (10 ml) the aqueous phase was separated and extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried (Na$_2$SO$_4$), filtered, and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography on neutral alumina with *n*-hexane–ethyl acetate (3 : 2) as eluent to yield **7a** as a brown solid (0.21 g, 51%), mp >90 °C (decomp.); δ_H (400 MHz, CDCl$_3$)[22] 2.79 (1 H, d with fine-coupling, ^2J 16.0, 6-H), 2.90, 2.99 (2 × 6 H, 2 s, 2 × NMe$_2$), 3.07 (1 H, dd, ^2J 16.0, ^3J 5.7, 6-H), 4.38 (1 H, br d, J 5.7, 5-H), 5.83 (1 H, dd, J 10.0, J 0.9, 2-H), 6.47 (2 H, AA′BB′ system with J_{AB} 9.0, ArH), 6.67 (2 H, AA′BB′ system with J_{AB} 8.8, ArH), 6.87 (2 H, AA′BB′ system with J_{AB} 9.0, ArH), 7.07 (2 H, AA′BB′ system with J_{AB} 8.8, ArH), 7.16–7.21 (1 H, m, ArH), 7.22–7.29 (4 H, m, ArH), 7.47 (1 H, dd, J 10.0, J 1.4, 3-H); δ_C (100 MHz, CDCl$_3$)[22] 40.08, 40.19 (2 q, 2 × NMe$_2$), 45.53 (d, C-5), 45.65 (t, C-6), 110.91, 111.02 (2 d, Ar), 124.85 (d, C-2), 126.14, 127.78 (2 d, Ar), 128.38 (br s), 128.42 (d, Ar), 129.23, 128.88 (2 s), 132.66, 130.93 (2 d, Ar), 143.66 (s), 148.14 (d, C-3), 149.90, 150.27 (2 s), 198.06 (s, C-1); *m/z* (EI): 422 (M$^+$, 100%), 345 (6), 253 (11).

4-[Bis(4-dimethylaminophenyl)methylene]-5-(4-dimethylamino-phenyl)cyclohex-2-enone (7b)

A mixture of **1d**–BF$_4$ (0.50 g, 1.03 mmol) and diene **2c** (0.40 ml, 0.36 g, 2.1 mmol) in dichloromethane (10 ml) was stirred for 1 h at ambient temperature. Work-up and chromatographic purification as described for the isolation of **7a** gave an orange oil which could be crystallised from a dichloromethane–pentane mixture to give yellow needles of **7b** (35.8 mg, 8%); mp >92 °C (decomp.); δ_H (400 MHz, CDCl$_3$)[22] 2.74–3.10 (2 H, m, superimposed by signals of NMe$_2$, 6-H$_2$), 2.918, 2.920, 3.004 (3 × 6 H, 3 s, 3 × NMe$_2$), 4.31 (1 H, br d, J 4.7, 5-H), 5.81 (1 H, dd, J 10.0, J 0.9, 2-H), 6.50 (2 H, AA′BB′ system with J_{AB} 9.0, ArH), 6.66–6.69 (4 H, m, ArH), 6.94 (2 H, AA′BB′ system with J_{AB} 9.0, ArH), 7.07 (2 H, AA′BB′ system with J_{AB} 9.0, ArH), 7.12 (2 H, AA′BB′ system with J_{AB} 8.8, ArH), 7.42 (1 H, dd, J 10.0, J 1.4, 3-H); δ_C (100 MHz, CDCl$_3$)[22] 40.20, 40.31, 40.69 (3 q, 3 × NMe$_2$), 44.61 (d, C-5), 45.81 (t, C-6), 111.03, 111.12, 112.89 (3 d, Ar), 124.94 (d, C-2), 128.49 (d, Ar), 129.22, 129.43, 129.59 (3 s), 131.12 (d, Ar), 131.54 (s), 132.73 (d, Ar), 148.15 (d, C-3), 149.02, 149.16, 149.90, 150.25 (4 s), 198.76 (s, C-1); *m/z* (EI) 465 (M$^+$, 100%), 253 (15) (HRMS: Found *m/z* 465.2747. C$_{31}$H$_{35}$N$_3$O requires 465.2780).

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