$[2^{+}+4]$ Cycloadditions of Iminium Ions − Concerted or Stepwise Mechanism of Aza Diels−Alder Reactions?

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Dedicated to Professor Rudolf Knorr on the occasion of his 65th birthday

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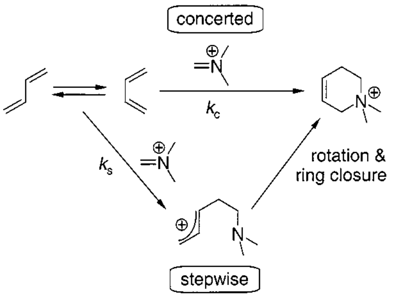
The *N*,*N*-dimethylmethyleneammonium ion **1** reacts regio- and stereoselectively with the 1,3-dienes **2a**–**2f** to yield the 1,2,5,6-tetrahydropyridinium ions **3**. The kinetics of these hetero Diels–Alder reactions, which have been followed by dilatometry and ^{1}H-NMR spectroscopy, obey second-order rate laws. Since the observed rate constants are only 30–300 times larger than those calculated for the stepwise process by the linear free-enthalpy relationship $\lg k = s\,(E + N)$, it is concluded that these cycloadditions proceed in a stepwise manner or through pericyclic transition states that are not significantly stabilized by the concerted formation of two new σ-bonds. In contrast, the reaction of the iminium ion **1** with cyclopentadiene (**2g**) yields 2,2-dimethyl-2-azoniabicyclo[2.2.1]hept-5-ene (**3g**) 2×10^4 times more rapidly than predicted for the stepwise cycloaddition process, indicating a free enthalpy of concert of 27 kJ mol^{-1}.

Introduction

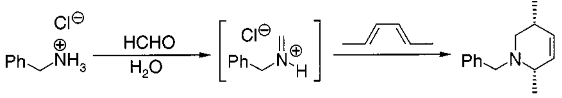
Whereas the reactions of iminium ions with olefins, silyl enol ethers, and arenes[1] usually proceed with formation of *one* new CC bond, *two* new bonds can be obtained in the reactions with conjugated dienes (aza Diels−Alder reactions).[2] Aqueous versions of these reactions, where three components viz. an aldehyde, an ammonium salt, and a 1,3-diene are combined to produce six-membered heterocycles have attracted much interest.[3−5]

Early examples of aza Diels−Alder reactions of dialkylmethyleneammonium ions with 2,3-dimethylbutadiene and isoprene in aprotic solvents were reported by Böhme et al.[6] and Babayan et al.,[7] respectively. Katritzky and Gordeev have recently re-investigated and supplemented this work.[8]

In order to ascertain whether the $[2^{+}+4]$ cycloadditions of iminium ions proceed according to concerted or stepwise mechanisms (Scheme 1), the stereospecificities of the reactions with 1,4-disubstituted 1,3-dienes have been assessed. Only one diastereomer could be detected following the cycloaddition of the in situ generated benzylmethyleneammonium ion to (*E*,*E*)-2,4-hexadiene[3] (Scheme 2).



Scheme 1



Scheme 2

Though concerted mechanisms are suggested by this and related experiments, the observed stereospecificities of these reactions do not give any information about the relative activation energies associated with the concerted and the corresponding stepwise processes. The difference between these energies is of interest since in cases where there is only a slight preference for the concerted over the stepwise mechanism, a minute variation of the system (substituents, reaction conditions) may give rise to a change of mechanism. In the case of a high energy of concert, however, it can be concluded that the concerted cycloaddition mechanism will generally be preferred. In the present work, we have probed this matter by carrying out dilatometric and NMR kinetic studies of the Diels−Alder reactions of preformed methyleneammonium ions[9] with 1,3-dienes and comparing the observed rate constants with those predicted for the corresponding stepwise processes.

Results

Products

The dienes **2a**−**2g** were added to suspensions of the *N*,*N*-dimethylmethyleneammonium salts **1**-Y in aprotic solvents

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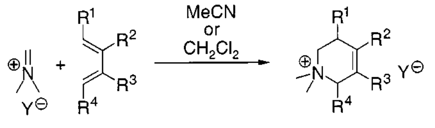
(acetonitrile for iminium halides, dichloromethane for iminium hexachloroantimonates) under exclusion of moisture. Due to the low solubilities of the iminium salts in these solvents, the progress of the reactions could conveniently be followed by observing the dissolution of the solids. Analytically pure hexachloroantimonates **3**-$SbCl_6$ were obtained without further purification on removal of the volatile reagents and solvents. Up to three recrystallizations were necessary, however, to obtain the tetrahydropyridinium halides **3**-Cl and **3**-Br in an analytically pure state (Scheme 3).



1-Y **2** **3**-Y

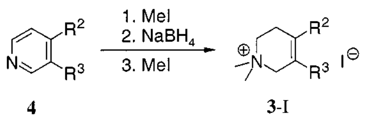
		R^1, R^2, R^3, R^4		Yield[a] [%]
1-Cl	**2a**	H, H, H, H	**3a**-Cl	13 (22)
1-Br	**2b**	H, Me, H, H	**3b**-Br	66 (98)
1-$SbCl_6$	**2b**	H, Me, H, H	**3b**-$SbCl_6$	81
1-Br	**2c**	H, H, H, Me	**3c**-Br	13 (86)
1-Br	**2d**	H, Me, Me, H	**3d**-Br	73 (98)
1-Br	**2e**	Me, H, H, Me	**3e**-Br	58 (93)
1-Br	**2f**	Ph, H, H, Ph	**3f**-Br	51 (95)
1-$SbCl_6$	**2g**	Cyclopentadiene	**3g**-$SbCl_6$	85

[a] Yields refer to recrystallized, analytically pure compounds, values given in parentheses correspond to the yields of the crude products; NMR spectra using an internal standard proved a purity of ca. 90% for the crude products.

Scheme 3

In analogy to Grieco's experiments in protic solvents[3] (Scheme 2), ^{1}H-NMR analysis of the crude products of the reactions of the preformed *N*,*N*-dimethylmethyleneammonium bromide (**1**-Br) with (*E*,*E*)-2,4-hexadiene (**2e**) and (*E*,*E*)-1,4-diphenyl-1,3-butadiene (**2f**) showed the presence of only one diastereomer in each case, consistent with these cycloadditions proceeding in a concerted manner under aprotic conditions as well.

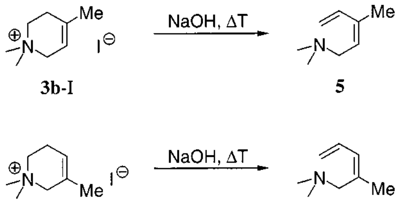
The cycloadducts **3a**-I, **3b**-I, and **3d**-I were synthesized independently, as was **3h**-I, a regioisomer of **3b**-I, the $[2^++4]$ cycloadduct of $\mathbf{1}^+$ and isoprene (**2b**). According to Birch and McKague,[10] the methyl-substituted pyridines **4a**, **4b**, **4d**, and **4h** could easily be transformed to the corresponding 1,2,5,6-tetrahydropyridine derivatives in three steps (Scheme 4). The NMR spectra of the cycloadducts $\mathbf{3a}^+$, $\mathbf{3b}^+$, and $\mathbf{3d}^+$ matched those of the corresponding products synthesized independently. ^{1}H-NMR studies of mixtures of the two regioisomers **3b**-I and **3h**-I showed that as little as 3−4% of **3h**-I could be detected besides **3b**-I.



4 **3**-I

	R^2	R^3	
4a	H	H	**3a**-I
4b	Me	H	**3b**-I
4d	Me	Me	**3d**-I
4h	H	Me	**3h**-I

Scheme 4



Scheme 5

Apparently, the $[2^++4]$ cycloaddition of $\mathbf{1}^+$ to isoprene **2b** leads to only one regioisomer (the "*para*" isomer).[11] Analogously for the combination $\mathbf{1}^+$ + piperylene (**2c**) yields only the 1,1,2-trimethyl-1,2,5,6-tetrahydropyridinium salt $\mathbf{3c}^+$ ("*ortho*" isomer).

The constitutions of $\mathbf{3b}^+$ and $\mathbf{3h}^+$ could be further verified by submitting them to Hofmann elimination,[7] which yielded the pentadiene derivatives **5** and **6**, respectively (Scheme 5). These could easily be distinguished through the multiplicities of the ^{1}H-NMR signals of their NCH_2 groups (doublet for **5** and singlet for **6**).

Dilatometric Kinetic Measurements

Generally speaking, [2+4] cycloadditions are associated with high negative values for the reaction volume ΔV. A wealth of relevant ΔV data is available in the literature,[12] with values typically ranging from −30 to −40 $cm^3\ mol^{-1}$. Therefore, the dilatometric technique, by means of which volume contractions can be followed, may be employed for kinetic measurements. We used the method originally published by Goering and Jacobson,[13] and described in detail in Huisgen's contribution on 1,3-dipolar cycloadditions of nitrones.[14] To evaluate the data, we applied the Guggenheim method,[15] for which knowledge of the initial concentrations of reactants or infinity readings of a physical property are not required. The second-order rate constants collected in Table 1 cover a wide range of the reaction (15−90% conversion) and were found to be well-reproducible.

Table 1. Rate constants for the cycloadditions of the iminium salt **1**-Br to the 1,3-dienes **2a**−**2e** determined by dilatometry (in CH_3CN, 40 °C)

$c_o(\mathbf{1}^+)$ [mol L^{-1}]	$c_o(\mathbf{2})$ [mol L^{-1}]	Conversion [%]	k_{obs} [L mol^{-1} s^{-1}]
1,3-Butadiene (**2a**)			
1.19×10^{-2}	8.88×10^{-1}	3 ... 88	7.00×10^{-6}
1.20×10^{-2}	8.89×10^{-1}	3 ... 91	7.30×10^{-6}
Isoprene (**2b**)			
1.18×10^{-2}	2.64×10^{-1}	14 ... 91	2.70×10^{-4}
1.14×10^{-2}	2.64×10^{-1}	15 ... 92	2.70×10^{-4}
(*E*)-1,3-Pentadiene (**2c**)			
1.27×10^{-2}	2.72×10^{-1}	21 ... 92	3.00×10^{-4}
1.26×10^{-2}	2.77×10^{-1}	20 ... 90	3.10×10^{-4}
2,3-Dimethylbutadiene (**2d**)			
2.28×10^{-2}	1.36×10^{-1}	14 ... 88	6.40×10^{-4}
2.45×10^{-2}	1.26×10^{-1}	14 ... 90	6.50×10^{-4}
(*E*,*E*)-2,4-Hexadiene (**2e**)			
1.27×10^{-2}	1.88×10^{-1}	2 ... 90	9.3×10^{-5}
1.29×10^{-2}	1.89×10^{-1}	9 ... 88	9.4×10^{-5}

Table 2. Rate constants for the cycloadditions of the iminium salts **1**-Y to the 1,3-dienes **2b**, **2d**, and **2g** determined by ^{1}H-NMR spectroscopy (in CD_3CN, 20 °C)

1-Y	$c_o(\mathbf{1}^+)$ [mol L^{-1}]	$c_o(\mathbf{2})$ [mol L^{-1}]	Conversion [%]	k_{obs} [L mol^{-1} s^{-1}]
Isoprene (**2b**)				
1-$AlCl_4$	2.63×10^{-1}	1.21	3 ... 60	8.86×10^{-5}
1-$AlCl_4$	3.31×10^{-1}	1.40	3 ... 56	7.31×10^{-5}
1-$SbCl_6$	2.11×10^{-1}	1.50	4 ... 72	1.11×10^{-4}
2,3-Dimethylbutadiene (**2d**)				
1-$AlCl_4$	6.59×10^{-2}	5.89×10^{-1}	8 ... 74	3.27×10^{-4}
1-$AlCl_4$	2.37×10^{-1}	8.74×10^{-1}	9 ... 86	3.86×10^{-4}
1-$SbCl_6$	1.56×10^{-1}	7.65×10^{-1}	6 ... 86	2.45×10^{-4}
Cyclopentadiene (**2g**)				
1-$SbCl_6$	6.06×10^{-2}	2.89×10^{-1}	10 ... 87	1.58×10^{-1}[a]
1-$SbCl_6$	5.59×10^{-2}	2.97×10^{-1}	11 ... 92	1.64×10^{-1}[a]
1-$SbCl_6$	6.02×10^{-2}	2.66×10^{-1}	14 ... 83	1.31×10^{-1}[a]

[a] Rapid-injection NMR measurements.

NMR Kinetic Measurements

In order to confirm the rate constants determined by dilatometry by an independent method and to study the influence of the counterions, the reactions of the iminium hexachloroantimonate **1**-$SbCl_6$ and of the tetrachloroaluminate **1**-$AlCl_4$ with isoprene (**2b**) and 2,3-dimethylbutadiene (**2d**) were investigated by ^{1}H-NMR spectroscopy. While these cycloadditions could be studied by conventional NMR techniques, the faster reactions with cyclopentadiene (**2g**) were followed with a "rapid-injection NMR"[16] device. In agreement with the results of the dilatometric investigations and in analogy to other reactions of carbocations with π-nucleophiles, the reactions of the iminium salts **1**-Y with the dienes **2b**, **2d**, and **2g** were found to follow second-order kinetics, first-order with respect to $\mathbf{1}^+$ and first-order with respect to the diene **2** (Table 2).

Discussion

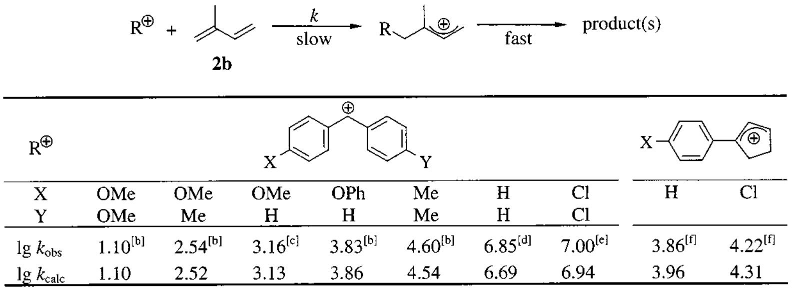
In previous work it has been shown that the reactions of carbocations with alkenes, dienes, and other uncharged nucleophiles follow the linear free-enthalpy relationship [Equation (1)], where the nucleophiles are characterized by the parameters N and s, and the electrophilicities of the carbocations are expressed by the value of E.[17]

$$\lg k_{20\,°\mathrm{C}} = s\,(E + N) \qquad (1)$$

Even though this equation has been applied to a wide variety of structurally diverse electrophiles and nucleophiles, the predicted rate constants have generally proved to be reliable with an accuracy better than a factor of 10−100, as shown for the reactions with isoprene (**2b**) in Scheme 6.

Since the hypothetical reaction of the iminium ion $\mathbf{1}^+$ with isoprene (**2b**) to yield the allyl cation $\mathbf{7}^+$ ($\mathbf{1}^+ + \mathbf{2b} \rightarrow \mathbf{7}^+$) also represents an electrophile−nucleophile combination in which *one* new bond is produced in the rate-determining step, one can expect that its rate should be adequately predicted by Equation (1). From the kinetic data and the calculated free enthalpies of the reactants, intermediates, and products (AM1 calculations[23]), the energy profile of this [2^++4] cycloaddition has been constructed in the following way.

Let us assume that the experimental free enthalpy of activation $\Delta G^{\ddagger}_{obs}$ (20 °C) = 94 kJ mol^{-1} represents the barrier associated with the concerted reaction path depicted in the left part of Figure 1. Equation (1) and the electrophilicity and nucleophilicity parameters of the reactants [$E(\mathbf{1}^+) = -7.0$,[24] $N(\mathbf{2b}) = 1.12$,[17a] $s(\mathbf{2b}) = 0.98$[17a]] were then used to calculate the rate constant for the formation of $\mathbf{7}^+$ from $\mathbf{1}^+$ and **2b**, i.e. the first step of the stepwise reaction [$\Delta G^{\ddagger}_{step}$ (20 °C) = 104 kJ mol^{-1}]. The allyl cation $\mathbf{7}^+$ is calculated (by AM1) to be 46.6 kJ mol^{-1} higher in $\Delta_f G^0$ than the reactants $\mathbf{1}^+$ and *s-trans*-**2b**. Isomerization $\mathbf{7}^+ \rightarrow \mathbf{9}^+$ might be achieved directly through allyl rotation for which



X	OMe	OMe	OMe	OPh	Me	H	Cl	H	Cl
Y	OMe	Me	H	H	Me	H	Cl		
lg k_{obs}	1.10[b]	2.54[b]	3.16[c]	3.83[b]	4.60[b]	6.85[d]	7.00[e]	3.86[f]	4.22[f]
lg k_{calc}	1.10	2.52	3.13	3.86	4.54	6.69	6.94	3.96	4.31

[a] Eq. (1), E-parameters for the carbocations were taken from ref.[17a]. – [b] From ref.[18]. – [c] From ref.[19]. – [d] In 1,2-dichloroethane, from ref.[20]. – [e] In acetonitrile, from ref.[21]. – [f] From ref.[22].

Scheme 6. Comparison of observed and calculated[a] rate constants for the reactions of carbocations with isoprene (**2b**, $N = 1.12$, $s = 0.98$) at 20 °C in CH_2Cl_2

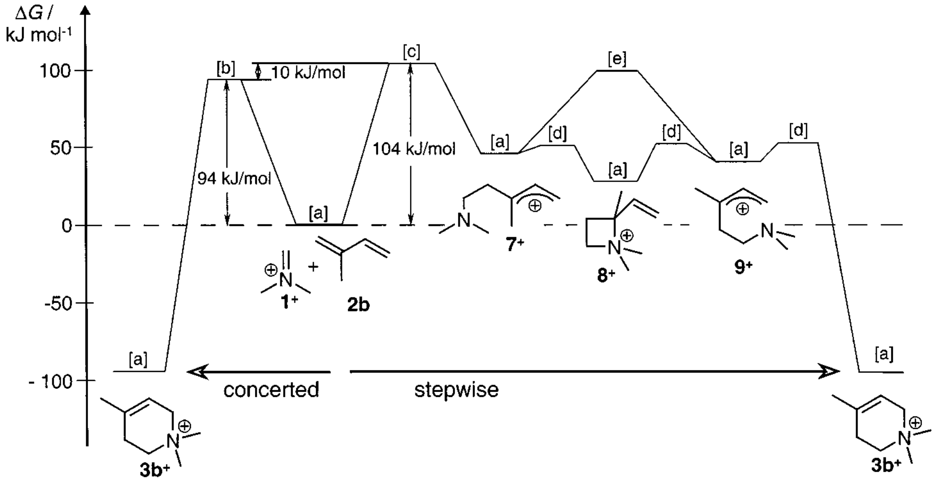


Figure 1. Energy profile for the concerted (left) and the stepwise Diels−Alder reaction (right) of *N*,*N*-dimethylmethyleneammonium (1^+) with isoprene (**2b**) (T = 20 °C): [a]: From AM1 calculations. − [b]: Barrier obtained from kinetic measurements (see Table 2). − [c]: Barrier calculated by Equation (1). − [d]: Unknown barrier. − [e]: Rotational barrier of the 1,1-dimethylallyl cation in superacid solution (Equation 19 in ref.[25a])

a barrier of approximately 53 kJ mol^{-1} can be assumed.[25] Alternatively, this isomerization might proceed through a cyclization−ring-opening sequence via the intermediate 8^+ ($\Delta_f G^0$ = 27.9 kJ mol^{-1}, as calculated by AM1). Though the barriers associated with the processes $7^+ \rightarrow 8^+ \rightarrow 9^+$ are probably lower than that for rotation of the allyl cation, Figure 1 shows that the decomposition of 7^+ with regeneration of 1^+ and **2b** would even be slower than the stereomutation $7^+ \rightarrow 9^+$ through allyl group rotation. The stepwise cycloaddition sequence would be terminated by ring-closure of 9^+ to give the 1,2,5,6-tetrahydro-1,1,4-trimethylpyridinium ion $3b^+$ ($\Delta_f G^0$ = −94.4 kJ mol^{-1}, as calculated by AM1). Since $3b^+$ is almost free of strain, the high N values of amines ($N > 13$[26a]) and the high E values of 1,1-dialkylated allyl cations (E = 8.0−8.5[26b]) lead us to the conclusion that the 6-*endo-trig* cyclization $9^+ \rightarrow 3b^+$ proceeds extremely rapidly. Consequently, the formation of 7^+ has to be considered as the rate-determining step of this stepwise cycloaddition.

In an alternative stepwise process, which may account for the observed stereospecificities,[27] 9^+ is produced directly from 1^+ and the *s-gauche* conformer of isoprene (**2b**).

With the assumption that the observed rate constant k_{obs} corresponds to the concerted reaction, and that the rate constant for the rate-determining step of the stepwise reaction k_{step} (= k_{calc}) can be calculated from Equation (1), the "free enthalpy of concert" is given by Equation (2).

$$\Delta G_{concert} = RT \ln(k_{obs}/k_{calc}) \qquad (2)$$

The entries in Table 3 demonstrate that k_{obs} is only slightly larger than k_{calc} (= k_{step}) for the reactions of the iminium ion 1^+ with the conjugated dienes **2a**−**2e**. Since in these cases the deviation between k_{calc} and k_{obs} barely exceeds the error limit associated with Equation (1), one can conclude that the transition state is not noticeably stabilized by the simultaneous formation of two new σ-bonds. The kinetic data are indicative of a stepwise mechanism or a concerted pathway, in which the formation of the C−N σ-bond lags far behind the formation of the new C−C bond. Ab initio MO calculations at the 3-21G level on the cycloaddition of 1,3-butadiene (**2a**) to $H_2C{=}NH_2^+$ revealed a transition structure, in which the new C−C and C−N bonds lengths amounted to 1.919 Å and 3.058 Å, respectively.[28]

Table 3. "Free enthalpies of concert" $\Delta G_{concert}$ [kJ mol^{-1}] for Diels−Alder reactions of the iminium ion 1^+ at 20 °C

Diene[a]	lg k_{obs}	lg k_{step} [b]	k_{obs}/k_{step}	$\Delta G_{concert}$
1,3-Butadiene (**2a**)	−5.70[c]	−8.15	282	13.7
Isoprene (**2b**)	−4.04	−5.76	53	9.7
(*E*)-1,3-Pentadiene (**2c**)	−3.95[c]	−5.45	32	8.5
2,3-Dimethylbutadiene (**2d**)	−3.50	−5.63	135	12.0
(*E*,*E*)-2,4-Hexadiene (**2e**)	−4.50[c]	−6.36	73	10.5
Cyclopentadiene (**2g**)	−0.82	−5.13	20 417	26.9

[a] N (and s) values of **2a**, **2b**, **2c**, **2d**, and **2e**: −1.15 (1.00), 1.22 (0.98), 1.55 (1.00), 1.37 (1.00), 1.22 (1.10), from ref.[17a]; **2g**: 2.25 (1.08), from ref.[30]. − [b] From Equation (1). − [c] For **2a**, **2c**, and **2e** rate constants k_{obs} (20 °C) were calculated with an estimated $\Delta S^{\ddagger}$ = −210 J mol^{-1} K^{-1}, which was derived from the temperature dependence of the reactions of **2b** and **2d** with 1^+ (Tables 1 and 2).

In contrast, the cycloaddition of 1^+ to cyclopentadiene (**2g**) is seen to be much faster than calculated for a stepwise reaction (Table 3). This observation rules out the stepwise mechanism and shows that the transition state of the pericyclic reaction is 27 kJ mol^{-1} lower in energy than that of the hypothetical stepwise process. The preference for the concerted reaction of cyclopentadiene (**2g**) may be due to the *s-cis*-fixed diene system and the favorable 1,4-distance.[29]

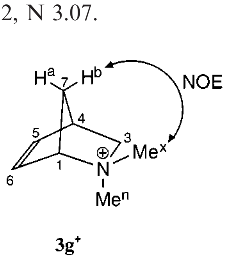
It can be concluded that the aza Diels−Alder reactions of the *N*,*N*-dimethylmethyleneammonium ion 1^+ with the acyclic 1,3-dienes **2a**−**2e** proceed via transition states that closely resemble those yielding intermediate allyl cations. Only in the case of the reaction with the *s-cis*-fixed cyclopentadiene (**2g**) has unequivocal evidence for a pericyclic transition state been obtained.

Experimental Section

General: All reactions were carried out under dry nitrogen in carefully dried Schlenk tubes. Acetonitrile and dichloromethane were freshly distilled from CaH_2 prior to use. *N,N*-Dimethylmethyleneammonium hexachloroantimonate (**1**-$SbCl_6$) and tetrachloroaluminate (**1**-$AlCl_4$) were prepared from commercially available **1**-Cl (Merck−Schuchardt) by the procedure of Knoll and Krumm.[31] The bromide **1**-Br was obtained from bis(dimethylamino)methane and dibromomethane by a procedure described by Böhme et al.[32] − NMR: Bruker WH90 (90 MHz and 22.6 MHz, for ^1H and ^{13}C NMR, respectively) and Bruker ARX 300 (300 MHz and 75.5 MHz, for ^1H and ^{13}C NMR, respectively). For ^1H and ^{13}C NMR, D_2O as solvent, $Me_3SiCD_2CD_2CO_2Na$ as internal standard; CD_3OD as solvent, tetramethylsilane as internal standard; [D_3]acetonitrile as solvent δ_H (residual CD_2HCN) = 1.93, δ_C = 1.30. Coupling constants $J_{N,H}$ and $J_{N,C}$ refer to spin−spin coupling of ^{14}N (I = 1) with ^1H and ^{13}C, respectively.[33] − MS: Varian MAT 311 A.

1,2,5,6-Tetrahydro-1,1,4-trimethylpyridinium Hexachloroantimonate (3b-$SbCl_6$): Diene **2b** (0.800 mL, 8.00 mmol) was added to a stirred suspension of **1**-$SbCl_6$ (1.42 g, 3.62 mmol) in dichloromethane (15 mL) at ambient temperature. Dissolution of the iminium salt was complete after stirring for 27 h. Evaporation of all volatile compounds in vacuo without heating yielded **3b**-$SbCl_6$ (1.35 g, 81%) as a colorless powder; dec. > 185 °C. − ^1H NMR (CD_3CN, 300 MHz): δ = 1.78 (br. s, 3 H, 4-Me), 2.37 (br. s, 2 H, 5-H), 3.02 (s, 6 H, NMe_2), 3.36 (t, J = 6.3 Hz, 2 H, 6-H), 3.73 (br. s, 2 H, 2-H), 5.37 (br. s, 1 H, 3-H). − ^{13}C NMR (CD_3CN, 75.5 MHz): δ = 22.3 (q, 4-Me), 26.5 (t, C-5), 52.4 (qt, $J_{N,C}$ = 4 Hz, NMe_2), 60.1 (t, C-6), 62.0 (tt, $J_{N,C}$ = 3 Hz, C-2), 113.5 (d, C-3), 134.0 (s, C-4). Signal assignments were based on 2D-NOESY, $^1H,^1H$ COSY, and $^1H,^{13}C$ COSY experiments. − $C_8H_{16}Cl_6NSb$ (460.7): calcd. C 20.86, H 3.50, N 3.04; found C 21.37, H 3.56, N 3.15.

2,2-Dimethyl-2-azoniabicyclo[2.2.1]hept-5-ene Hexachloroantimonate (3g-$SbCl_6$): Cyclopentadiene **2g** (0.19 mL, 2.3 mmol) was added to a stirred suspension of **1**-$SbCl_6$ (450 mg, 1.15 mmol) in dichloromethane at ambient temperature. Owing to the low solubility of **3g**-$SbCl_6$, the mixture remained heterogeneous. After 10 min, all volatile compounds were evaporated in vacuo to yield **3g**-$SbCl_6$ (0.45 g, 85%) as a colorless powder; dec. > 150 °C. − ^1H NMR (CD_3CN, 300 MHz): δ = 1.94−1.99 (m, partially obscured by the solvent signal, 1 H, 7-H^a), 2.20 (d with fine coupling, J = 11.1 Hz, 1 H, 7-H^b), 2.85 (s, 3 H, NMe^n), 2.87 (dd, J = 10.7 Hz, 2.3 Hz, 1 H, 3-H), 3.23 (s, 3 H, NMe^x), 3.46 (m_c, 1 H, 4-H), 3.54 (dd, J = 10.8 Hz, 2.9 Hz, 1 H, 3-H), 4.56 (m_c, 1 H, 1-H), 6.40 (dd, J = 5.6 Hz, 2.8 Hz, 1 H, 6-H), 6.80 (m_c, 1 H, 5-H). − ^{13}C NMR (CD_3CN, 75.5 MHz): δ = 45.8 (d, C-4), 47.8 (t, C-7), 52.6 (qt, $J_{N,C}$ = 4.4 Hz, NMe^n), 54.9 (qt, $J_{N,C}$ = 3.7 Hz, NMe^x), 65.8 (tt, $J_{N,C}$ = 4.8 Hz, C-3), 81.1 (d, C-1), 132.1 (d, C-6), 144.9 (d, C-5). Signals were assigned by comparisons with the spectra of analogous compounds[4b,34] and additional 2D-NOE experiments. − MS (FD, 0−20 mA): m/z (%) = 126 (3), 125 (22), 124 (100) [M − $SbCl_6^-$]. − $C_8H_{14}Cl_6NSb$ (458.7): calcd. C 20.95, H 3.08, N 3.05; found C 20.92, H 3.02, N 3.07.



$3g^+$

General Procedure for Diels−Alder Reactions of the Iminium Halides 1-Y with the Dienes 2: At ambient temperature, one equivalent of the diene **2** was added to a stirred suspension of the iminium salt **1**-Y in acetonitrile. After 1 h, the mixture was gently heated in a stoppered round-bottomed flask and the stirring was continued until **1**-Y had completely dissolved. Owing to the low solubility of **1**-Br (and **1**-Cl), reaction times of several days were necessary. Thereafter, methanol (10 mL) was added in order to convert the remaining iminium salt to the corresponding N,O-acetal. Stirring was continued for 24 h and then the volatile components of the mixture were evaporated. The residue was washed with pentane (3 × 25 mL) and dried in vacuo. Up to three recrystallizations of the crude products were necessary in order to obtain the analytically pure 1,2,5,6-tetrahydropyridinium salts **3**-Y.

1,2,5,6-Tetrahydro-1,1-dimethylpyridinium Chloride (3a-Cl): Diene **2a** (29.2 g, 540 mmol) was added to a stirred suspension of **1**-Cl (16.4 g, 175 mmol) in acetonitrile (300 mL) at ambient temperature. After 1 h, the mixture was heated to 65 °C and maintained at this temperature for 16 d. Work-up according to the general procedure and crystallization from ethanol/acetone yielded **3a**-Cl (3.36 g, 13%); dec. 312 °C. − IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3010, 2980−2840, 1660, 1475, 1395, 1050, 1015, 985, 930 cm^{-1}. − ^1H NMR (D_2O, 90 MHz): δ = 2.54 (m_c, 2 H, 5-H), 3.15 (s, 6 H, NMe_2), 3.48 (t, J = 6.1 Hz, 2 H, 6-H), 3.90 (m_c, 2 H, 2-H), 5.77 (dm, J = 11 Hz, 1 H, 3-H), 6.06 (dm, J = 11 Hz, 1 H, 4-H). − ^{13}C NMR (CD_3OD, 22.6 MHz): δ = 22.5 (t, C-5), 52.6 (tq, $J_{N,C}$ = 4 Hz, NMe_2), 59.9 (tt, $J_{N,C}$ = 3 Hz, C-6), 62.0 (tt, $J_{N,C}$ = 3 Hz, C-2), 120.0 (d, C-3), 125.5 (d, C-4). − $C_7H_{14}ClN$ (147.7): calcd. C 56.94, H 9.56, N 9.49; found C 57.35, H 10.13, N 9.29.

1,2,5,6-Tetrahydro-1,1,4-trimethylpyridinium Bromide (3b-Br): Diene **2b** (838 mg, 12.3 mmol) was added to a stirred suspension of **1**-Br (1.15 g, 8.35 mmol) in acetonitrile (10 mL). After 1 h, the mixture was warmed to 40 °C and maintained at this temperature for 80 d. Work-up according to the general procedure and recrystallization from 2-propanol/acetone yielded **3b**-Br (1.14 g, 66%); m.p. 217.5−220 °C. − IR (KBr): $\tilde{\nu}$ = 3005, 2965−2860, 1685, 1485, 1450, 1415, 1090, 1040, 935, 915 cm^{-1}. − ^1H NMR (D_2O, 90 MHz): δ = 1.80 (m_c, 3 H, 4-Me), 2.44 (m_c, 2 H, 5-H), 3.13 (s, 6 H, NMe_2), 3.47 (t, J = 6.2 Hz, 2 H, 6-H), 3.85 (m_c, 2 H, 2-H), 5.44 (m_c, 1 H, 3-H). − ^{13}C NMR (CD_3OD, 22.6 MHz): δ = 22.2 (q, 4-Me), 26.1 (t, C-5), 51.9 (tq, $J_{N,C}$ = 4 Hz, NMe_2), 59.7 (tt, $J_{N,C}$ = 3 Hz, C-6), 61.6 (tt, $J_{N,C}$ = 4 Hz, C-2), 113.1 (d, C-3), 133.6 (s, C-4). − NMR data are identical with those of **3b**-Cl prepared from **1**-Cl and diene **2b**. − $C_8H_{16}ClN$ (161.7): calcd. C 59.43, H 9.98, N 8.66; found C 59.64, H 10.08, N 8.81.

1,2,5,6-Tetrahydro-1,1,2-trimethylpyridinium Bromide (3c-Br): To a stirred suspension of **1**-Br (1.44 g, 10.4 mmol) in acetonitrile (8 mL), diene **2c** (743 mg, 10.9 mmol) was added and the resulting mixture was stirred for 1 h at ambient temperature. It was then warmed to 40 °C and maintained at this temperature for 54 d. Work-up according to the general procedure and recrystallization from 2-propanol yielded **3c**-Br (0.28 g, 13%); dec. 273 °C. − IR (KBr): $\tilde{\nu}$ = 3085, 3045, 3010, 2990−2850, 1665, 1490, 1450, 1435, 1415, 990, 955, 780, 710, 665 cm^{-1}. − ^1H NMR (D_2O, 90 MHz): δ = 1.44 (dt, J = 6.8 Hz, $J_{N,H}$ = 2.0 Hz, 3 H, 2-Me), 2.50 (m_c, 2 H, 5-H), 2.96, 3.16 (2 × s, 2 × 3 H, NMe_2), 3.50 (t, J = 6.0 Hz, 1 H, 6-H), 3.52 (t, J = 6.5 Hz, 1 H, 6-H), 4.11 (m_c, 1 H, 2-H), 5.62 (dm, J = 11 Hz, 1 H, 3-H), 6.00 (dm, J = 11 Hz, 1 H, 4-H). − ^{13}C NMR (D_2O, CH_3CN as internal standard, 22.6 MHz): δ = 15.3 (q, 2-Me), 21.9 (t, C-5), 45.7 (tq, $J_{N,C}$ = 4 Hz, NMe), 52.5 (tq, $J_{N,C}$ = 4 Hz, NMe), 59.6 (tt, $J_{N,C}$ = 3 Hz, C-6), 66.2 (d, C-2), 124.9 (d, C-4), 125.4 (d, C-3). − NMR data are identical with those of

3c-Cl prepared from **1**-Cl and diene **3c**. − $C_8H_{16}ClN$ (161.7): calcd. C 59.43, H 9.98, N 8.66; found C 59.43, H 9.99, N 8.66.

1,2,5,6-Tetrahydro-1,1,3,4-tetramethylpyridinium Bromide (3d-Br):[35] To a stirred suspension of **1**-Br (2.07 g, 15.0 mmol) in acetonitrile (8 mL), diene **2d** (1.27 g, 15.4 mmol) was added at ambient temperature. After stirring for 1 h, the reaction mixture was warmed to 40 °C and maintained at this temperature for 51 d. Work-up according to the general procedure and recrystallization from 2-propanol/acetone yielded **3d**-Br (2.41 g, 73%); m.p. 175.5−177 °C. − IR (KBr): $\tilde{\nu}$ = 3020, 3005, 3000, 2920−2860, 1690, 1485, 1480, 1450, 1435, 1415, 1000, 965, 925 cm^{-1}. − ^1H NMR (D_2O, 90 MHz): δ = 1.66 (m_c, 3 H, C-Me), 1.75 (m_c, 3 H, C-Me), 2.42 (m_c, 2 H, 5-H), 3.11 (s, 6 H, NMe_2), 3.43 (t, J = 6.1 Hz, 2 H, 6-H), 3.74 (m_c, 2 H, 2-H). − ^{13}C NMR (D_2O, CH_3CN as internal standard, 22.6 MHz): δ = 15.7 (q, C−Me), 17.6 (q, C−Me), 26.6 (t, C-5), 51.7 (tq, $J_{N,C}$ = 4 Hz, NMe_2), 59.1 (t, C-6), 64.5 (tt, $J_{N,C}$ = 3 Hz, C-2), 118.0 (s, C-3), 124.0 (s, C-4). − NMR data are identical with those of **3d**-Cl prepared from **1**-Cl and diene **2d**. − $C_9H_{18}ClN$ (175.7): calcd. C 61.52, H 10.33, N 7.97; found C 61.60, H 10.60, N 8.08.

1,2,5,6-Tetrahydro-1,1,2,5-tetramethylpyridinium Bromide (3e-Br): Diene **2e** (719 mg, 8.75 mmol) was added to a stirred suspension of **1**-Br (1.28 g, 9.27 mmol) in acetonitrile (20 mL). After stirring at room temperature for 80 d, work-up according to the general procedure and recrystallization from 2-propanol/acetone furnished **3e** (1.12 g, 58%); dec. 217 °C. − IR (KBr): $\tilde{\nu}$ = 3085, 3025−3000, 2990−2870, 1670−1620, 1480, 1460, 1385, 1090, 1030, 1000, 945, 920, 755 cm^{-1}. − ^1H NMR (D_2O, 90 MHz): δ = 1.10 (d, J = 6.6 Hz, 3 H, C-Me), 1.45 (dt, J = 6.8 Hz, $J_{N,C}$ = 1.8 Hz, 3 H, C-Me), 2.68−3.75 (m, 3 H, 5-H, 6-H), 3.08, 3.15 (2 × s, 2 × 3 H, NMe_2), 3.94 (m_c, 1 H, 2-H), 5.76−5.96 (m_c, 2 H, 3-H, 4-H). − ^{13}C NMR (D_2O, CH_3CN as internal standard, 22.6 MHz): δ = 16.8 (q, C-Me), 17.1 (q, C-Me), 27.3 (d, C-5), 51.4 (tq, $J_{N,C}$ = 4 Hz, NMe), 52.2 (tq, $J_{N,C}$ = 4 Hz, NMe), 60.2 (tt, $J_{N,C}$ = 3 Hz, C-6), 65.6 (td, $J_{N,C}$ = 3 Hz, C-2), 124.7 (d, C-3), 129.6 (d, C-4). − $C_9H_{18}BrN$ (220.2): calcd. C 49.10, H 8.24, N 6.36; found C 48.98, H 8.19, N 6.35.

1,2,5,6-Tetrahydro-1,1-dimethyl-2,5-diphenylpyridinium Bromide (3f-Br): To a stirred suspension of **1**-Br (7.89 g, 57.2 mmol) in acetonitrile (100 mL), diene **2f** (12.3 g, 59.6 mmol) was added. After stirring for 1 h at room temperature, the mixture was heated to 82 °C and maintained at this temperature for 1 d. Work-up according to the general procedure and recrystallization from water yielded **3f**-Br (10.0 g, 51%); dec. 186−188 °C. − IR (KBr): $\tilde{\nu}$ = 3085, 3045, 3030, 3005, 2955−2885, 1640, 1495, 1455, 960, 890, 760, 750, 710, 700 cm^{-1}. − ^1H NMR (CD_3OD, 90 MHz): δ = 2.77 (s, 3 H, NMe), 3.12−3.98 (m, 2 H, 6-H), 3.57 (s, 3 H, NMe), 4.20 (m_c, 1 H, 5-H), 5.31 (m_c, 1 H, 2-H), 6.04 (dm, J = 11 Hz, 1 H, 3-H), 6.38 (dm, J = 11 Hz, 1 H, 4-H), 7.34−7.77 (m, 10 H, phenyl). − ^{13}C NMR (CD_3OD, 22.6 MHz): δ = 38.9 (d, C-5), 52.0, 53.4 (2 × q, NMe_2), 60.4 (t, C-6), 72.8 (d, C-2), 124.4 (d, C-3), 129.0 (d, Ph), 130.3 (d, Ph), 132.0 (s, Ph), 132.1 (d, C-4), 132.9 (d, Ph), 139.1 (s, Ph). − $C_{19}H_{22}BrN$ (344.3): calcd. C 66.28, H 6.44, N 4.07; found C 66.05, H 6.34, N 4.01.

General Procedure for Independent Syntheses of the Cycloadducts 3a-I, 3b-I, 3d-I, and 3h-I (in analogy to ref.[10]**):** The appropriate pyridines **4a**, **4b**, **4d**, and **4h** were treated with an excess of methyl iodide in dry diethyl ether at 0 °C and the respective mixtures were kept for 5 d at ambient temperature. The colorless crystals of the pyridinium salts thus formed were filtered off, washed, and dried, and then dissolved in water without further purification. To these aqueous solutions, aqueous $NaBH_4$ solution was slowly added with external cooling with ice/water and the reaction was allowed to proceed for 2 h at 20 °C. The aqueous solution was then saturated with NaCl and extracted three times with diethyl ether. The combined extracts were dried with Na_2SO_4, concentrated to one-half of the original volume, and excess methyl iodide was added. After 1 h at room temperature, the tetrahydropyridinium salts **3**-I were filtered off and dried.

The tetrahydropyridinium iodides **3**-I were converted to the corresponding chlorides by passage through an anion-exchanger (Bio-Rad, analytical grade anion-exchange resin AG1-X10 mesh 200−400, chloride form). The tetrahydropyridinium chlorides, bromides, and iodides **3a**$^+$, **3b**$^+$, **3d**$^+$, and **3h**$^+$ thus obtained showed the same ^1H- and ^{13}C-NMR spectra. The cycloadducts and the products of the independent syntheses were seen to be identical on the basis of their ^1H- and ^{13}C-NMR spectra.

1,2,5,6-Tetrahydro-1,1-dimethylpyridinium Iodide (3a-I): A solution of pyridine **4a** (44.3 g, 560 mmol) in diethyl ether (175 mL) was treated with methyl iodide (99.4 g, 700 mmol) at ambient temperature. After reaction and isolation of the crystalline crude product (111.4 g, 90%; m.p. 116−117.5 °C), a portion of it (22.1 g, 100 mmol) was dissolved in water (125 mL). To this solution was added a solution of $NaBH_4$ (7.57 g, 200 mmol) in water (125 mL). After work-up as described in the general procedure, further methyl iodide (45.6 g, 321 mmol) was added. Recrystallization of the precipitated salt from methanol/diethyl ether yielded **3a**-I (8.85 g, 37%); dec. 269 °C. − $C_7H_{14}IN$ (239.1): calcd. C 35.16, H 5.90, N 5.86; found C 35.10, H 6.00, N 5.97.

1,2,5,6-Tetrahydro-1,1,4-trimethylpyridinium Iodide (3b-I): A solution of pyridine **4b** (18.6 g, 200 mmol) in diethyl ether (60 mL) was treated with methyl iodide (35.5 g, 250 mmol). After reaction, the crystalline pyridinium salt was isolated (47.0 g, 100%; m.p. 152−154 °C). A portion of the crude product (23.5 g, 100 mmol) was dissolved in water (125 mL) and to this solution was added a solution of $NaBH_4$ (7.57 g, 200 mmol) in water (125 mL). After work-up as described in the general procedure, further methyl iodide (45.6 g, 321 mmol) was added. Recrystallization of the precipitated salt from methanol/diethyl ether and ethanol/acetone yielded **3b**-I (8.35 g, 33%); m.p. 226−227 °C. − $C_8H_{16}IN$ (253.1): calcd. C 37.96, H 6.37, N 5.53; found C 38.19, H 6.23, N 5.47.

1,2,5,6-Tetrahydro-1,1,3,4-tetramethylpyridinium Iodide (3d-I): To a solution of the pyridine **4d** (10.7 g, 100 mmol) in diethyl ether (50 mL) was added methyl iodide (17.7 g, 125 mmol). After 5 d, the crystalline pyridinium salt (23.9 g, 96%; m.p. 123−124 °C) was isolated as described above and a portion of it (21.7 g, 87.1 mmol) was dissolved in water (100 mL). To this solution was added a solution of $NaBH_4$ (6.58 g, 174 mmol) in water (100 mL). After the addition of further methyl iodide (45.6 g, 321 mmol) and recrystallization of the precipitated salt from acetonitrile/acetone, **3d**-I (2.79 g, 12%) was obtained; m.p. 159−160 °C. − C_9H_8IN (267.2): calcd. C 40.46, H 6.79, N 5.24; found C 40.49, H 6.81, N 5.49.

1,2,5,6-Tetrahydro-1,1,3-trimethylpyridinium Iodide (3h-I): A solution of pyridine **4h** (52.2 g, 561 mmol) in diethyl ether (175 mL) was treated with methyl iodide (99.4 g, 700 mmol) to yield the crystalline pyridinium iodide (126.4 g, 96%; m.p. 92.5−95 °C). A portion of the crude salt (23.5 g, 100 mmol) was dissolved in water (125 mL), and to this solution was added a solution of $NaBH_4$ (7.57 g, 200 mmol) in water (125 mL). After work-up as described in the general procedure, further methyl iodide (45.6 g, 321 mmol) was added. Recrystallization of the precipitated salt from methanol/diethyl ether and ethanol/acetone yielded **3h**-I (7.34 g, 29%);

m.p. 146−150 °C. − IR (KBr): $\tilde{\nu}$ = 3035, 3025, 3015, 3005, 2980−2850, 1475, 1440, 1395, 1390, 1375, 1220, 1185, 1170, 985, 960, 920, 905, 845, 810, 730 cm^{-1}. − ^1H NMR (D_2O, 90 MHz): δ = 1.70−1.80 (m_c, 3 H, 3-Me), 2.33−2.65 (m_c, 2 H, 5-H), 3.14 (s, 6 H, NMe_2), 3.43 (t, J = 6.0 Hz, 2 H, 6-H), 3.75−3.89 (m_c, 2 H, 2-H), 5.66−5.82 (m, 1 H, 4-H). − ^{13}C NMR (D_2O, 22.6 MHz): δ = 19.6 (q, 3-Me), 20.9 (t, C-5), 51.7 (tq, $J_{N,C}$ = 4 Hz, NMe_2), 58.5 (tt, $J_{N,C}$ = 3 Hz, C-6), 63.7 (tt, $J_{N,C}$ = 3 Hz, C-2), 117.8 (d, C-4), 126.2 (s, C-3). − $C_8H_{16}IN$ (253.1): calcd. C 37.96, H 6.37, N 5.53; found C 38.04, H 6.40, N 5.57.

Hofmann Degradation of 3b-I and 3h-I According to Ref.:[7] 1,2,5,6-Tetrahydropyridinium iodide **3b**-I or **3h**-I was heated under reflux in aqueous NaOH solution for 40 h. Thereafter, the organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic phases were dried with Na_2SO_4. The solvent was removed in vacuo and the oily residue was distilled under reduced pressure to yield the tertiary amines **5** and **6** as liquids.

5: From **3b**-I (16.9 g, 66.8 mmol) and NaOH (8.04 g, 201 mmol) in H_2O (16 mL), **5** (2.95 g, 35%) was obtained; b.p. 54 °C/18 Torr (ref.[7]: 48 °C/11 Torr). − n_D = 1.4698 (ref.[7]: 1.4700). − IR (film): $\tilde{\nu}$ = 3095, 3020, 2980−2770, 1650, 1600 cm^{-1}. − ^1H NMR (neat, 90 MHz): δ = 1.79 (d, J = 1 Hz, 3 H, C−Me), 2.10 (s, 6 H, NMe_2), 2.93 (d, J = 7 Hz, 2 H, NCH_2), 4.88−5.36 (m, 2 H, $=CH_2$), 5.42 (t, J = 7 Hz, 1 H, CH_2CH), 6.77 (ddd, J = 17 Hz, 11 Hz, 1 Hz, 1 H, $-CH=CH_2$).

6: From **3h**-I (16.2 g, 64.0 mmol) and NaOH (5.36 g, 134 mmol) in H_2O (16 mL), **6** (2.86 g, 36%) was obtained; b.p. 54 °C/18 Torr. − n_D = 1.4697. − IR (film): $\tilde{\nu}$ = 3095, 3045, 2980−2730, 1650, 1600, 1325, 1295 cm^{-1}. − ^1H NMR (neat, 90 MHz): δ = 1.78 (s, 3 H, C−Me), 2.08 (s, 6 H, NMe_2), 2.85 (s, 2 H, NCH_2), 4.79−5.20 (m, 2 H, $=CH_2$), 5.93 (d, J = 11 Hz, 1 H, $-CH=C-Me$), 6.69 (ddd, J = 17 Hz, 11 Hz, 10 Hz, 1 H, $-CH=CH_2$).

Dilatometric Kinetic Measurements:[36] A known volume of an almost saturated stock solution of **1**-Br in dry CH_3CN was diluted with a known amount of dry CH_3CN and then a known amount of freshly distilled 1,3-diene **2** was added so that the concentrations of the reactants were as given in Table 1. The dilatometer was filled with the reaction mixture and then transferred to a thermostatted bath, the temperature of which was guaranteed to be constant to within ± 0.001 K. After 15 min, the change in volume was monitored over the conversion range indicated in Table 1. Generally, 40−50 readings were taken, which were evaluated using the Guggenheim method[15] to yield the rate constants listed in Table 1. Further details can be found in refs.[14,36]

^{1}H-NMR Kinetic Measurements: A known volume of a solution of an iminium salt in [D_3]acetonitrile was placed in an NMR tube under argon atmosphere. The tube was sealed with a rubber septum and placed in the spectrometer (ARX 300) in order to record a spectrum of the initial dienophile solution. Thereafter, the sample was removed from the magnet and a known volume of the neat diene was injected by means of a syringe. A homogeneous solution was obtained after shaking for ca. 10 s. The probe was then returned to the magnet and the acquisition of the spectra and the delay times were controlled by the routine "variable delay list" (VD list) of the spectrometer. The concentrations of the components at each point in time were calculated from the initial concentration of the diene and the observed conversion at that time. The actual temperature was determined from the chemical shift differences of the CH_3 and OH signals of a methanol sample (10% in $CDCl_3$) and the temperature was kept constant to within ± 0.3 K by means of a VT controller. For the rapid-injection NMR measurements (Varian VXR-400S, 400 MHz for ^1H NMR), a device as described by Bauer[16] was employed.

AM1 Calculations:[23] After optimization of the geometries, the thermodynamic properties at T = 20 °C were evaluated from THERMO calculations. Vibrations below 200 cm^{-1} were arbitrarily treated as internal rotations[37] and were omitted by using appropriate values for the TRANS keyword (Table 4).

Table 4. Results of the AM1 thermodynamic calculations (20 °C)

Molecule	TRANS[a]	$\Delta_f H^0$ [kJ mol^{-1}]	S^0 [J mol^{-1} K^{-1}]
$\mathbf{1}^+$	2	730.5	267.4
2b	2	97.2	288.7
$\mathbf{3b}^+$	4	670.1	340.2
$\mathbf{7}^+$	8	808.9	332.9
$\mathbf{8}^+$	4	793.1	342.5
$\mathbf{9}^+$	8	802.1	328.6

[a] Vibrations lower than 200 cm^{-1} were omitted by choosing appropriate TRANS values.

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