Ketene–Diene [4 + 2] Cycloaddition Products via Cation Radical Initiated Diels–Alder Reaction or Vinylcyclobutanone Rearrangement[1]

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Abstract: Whereas the thermal reaction of the aryl methyl ketenes **1a** and **1b** with **2** resulted, as anticipated, in the periselective formation of the vinylcyclobutanones **3–6**, the aminium ion salt initiated cycloaddition afforded selectively the Diels–Alder products **10** and **12**. The potential role of Brønsted and Lewis acids, the suitability of different one-electron oxidants, and the effect of reactant concentration, reaction time, and added neutral amines was tested. From the results it is deduced that in the aminium ion salt initiated reaction the diene cation radical reacts with a neutral ketene in a [3 + 2] cycloaddition. Additionally, a second approach to the all-carbon ketene/diene Diels–Alder products via the cation radical vinylcyclobutanone rearrangement was developed. Thus, **3a–6a** could be smoothly rearranged to the norbornenones **10a–12a**. Importantly, the stereochemical outcome depends on the individual isomer, covering the whole range from 100% retention to 100% inversion of configuration. With regard to the mechanism it is concluded that the rearrangement proceeds via a ring-opened distonic cation radical. The charge distribution in the intermediate cation radical and the energetics of the product cation radicals control the stereochemical outcome. The monocyclic vinylcyclobutanone **9** could be rearranged with 100% retention to the formal Diels–Alder product **14**. No rearrangement occurred with **7**. Although mechanistic results propose that the correct bond is cleaved in **7**[·+], formation of the corresponding norbornenone cation radical is presumably too slow because of energetic reasons.
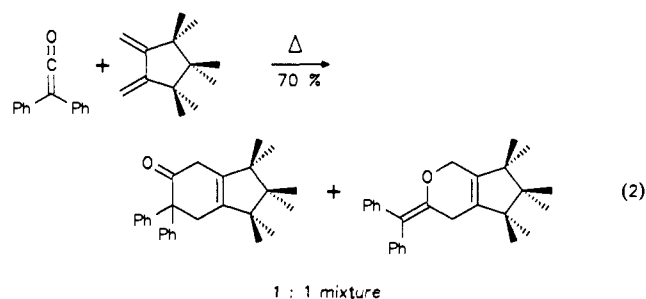
Introduction

Since Staudinger's pioneering work[2] at the beginning of this century, it is well-known that the reaction of ketenes with dienes results in the selective formation of [2 + 2] cycloadducts.[3] Remarkably, the corresponding Diels–Alder (DA) products are not formed at all (eq 1). While the unique ability of ketenes to

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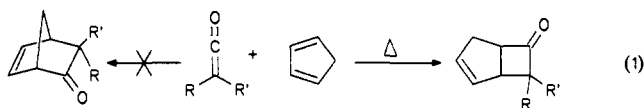
undergo [2 + 2] cycloadditions has provided a valuable, straightforward approach to cyclobutanone chemistry,[4] their potential as dienophiles in DA reactions has largely been neglected.[5] A rationale for the exclusive formation of [2 + 2] products in ketene/diene cycloadditions was provided by Woodward and Hoffmann that was based on orbital symmetry control.[6] Accordingly, a suprafacial, antarafacial [2ₛ + 2ₐ] cycloaddition mode can accommodate in an ideal way steric and electronic interactions while preserving orbital symmetry. Thus, as a result of kinetic control, vinylcyclobutanones and not the thermodynamically more stable DA products[7] are formed.

During recent years several ab initio calculations at various levels of theory that challenge the simple picture provided by the Woodward–Hoffmann theory have been published.[8] Most likely the cycloaddition proceeds in a [2 + 2 + 2] quasi pericyclic fashion exhibiting a highly asynchronous transition state. While the calculations disagree with the commonly accepted [2ₛ + 2ₐ] mechanism, they still require an orthogonal approach of both components in the cycloaddition. Hence, preventing the orthogonal approach by steric interactions is a feasible methodology to slow down or even totally impede the [2 + 2] cycloaddition mode. Applying this basic concept, Mayr was able for the first time to steer a ketene/diene cycloaddition (eq 2) directly to the all-carbon DA product. However, a drawback is that the cycloaddition also occurred at the C=O bond, thus affording a dihydropyrane adduct.[9]

(2)

1 : 1 mixture

Several years ago, we became fascinated by the possibility of controlling the [4 + 2] vs [3 + 2] periselectivity of ketene/diene cycloadditions by using cation radical catalysis. This approach seemed to be promising, since the cation radical catalyzed DA reaction,[10] as developed to a great extent by Bauld[11] during the last decade, has led to impressive rate accelerations in DA reactions while showing high chemo-, regio-, and stereoselectivity.[12]

(1) Electron Transfer Catalyzed Reactions. 3. Part 2: Gescheidt, G.; Lamprecht, A.; Heinze, J.; Schuler, B.; Schmittel, M.; Kiau, S.; Rüchardt, C. *Helv. Chim. Acta* **1992**, *75*, 1607.

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(3) Huisgen, R.; Otto, P. *Chem. Ber.* **1969**, *102*, 3475.

(4) (a) Ghosez, L.; O'Donnell, M. J. *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. 11, pp 79–140. (b) Brady, W. T. *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, 1980; pp 279–308. (c) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. (d) Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273.

(5) With the exception of [4 + 2] cycloaddition of ketenes with dienes containing heteroatoms: (a) Brady, W. T.; Agho, M. O. *J. Org. Chem.* **1983**, *48*, 5337. (b) Mazumdar, S. N.; Mahajan, M. P. *Tetrahedron* **1991**, *47*, 1473.

(6) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

(7) According to force field calculations using MM2-86, the reaction of bicyclo[3.2.0]hept-2-en-6-one to bicyclo[2.2.1]hept-5-en-2-one is exothermic by 9.4 kcal mol⁻¹: Allinger, N. L.; Flanagan, H. L. *J. Comput. Chem.* **1983**, *4*, 399.

(8) (a) Burke, L. A. *J. Org. Chem.* **1985**, *50*, 3149. (b) Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1988**, *110*, 5993. (c) Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1754. (d) Bernardi, F.; Bottoni, A.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1990**, *112*, 2106. (e) Seidl, E. T.; Schaeffer, H. F., III. *J. Am. Chem. Soc.* **1991**, *113*, 5195.

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Chart I

Figure 1. ^{1}H NMR difference NOE effects (indicated by double arrows) in vinylcyclobutanones 3a and 9 and in the [4 + 2] cycloadducts 10a, 12a, and 14.
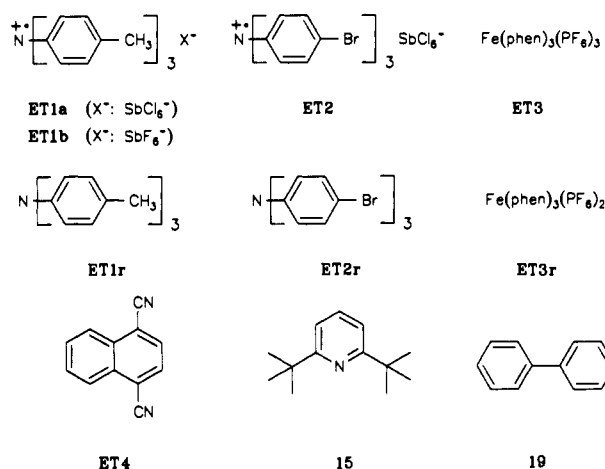
Consequently, one-electron oxidation seemed to be a viable strategy to overcome the symmetry constraints leading to [2 + 2] cyclo-adducts in ketene/diene cycloadditions and to open up a new way to DA reactions *with ketenes as dienophiles*. Very recently we have successfully used this approach in the reaction of *p*-anisyl- and *p*-tolylmethylketenes (**1a** and **1b**) with pentamethylcyclo-pentadiene (**2**).[13] Our choice of the model compounds had mainly been influenced by the requirement to match the oxidation po-tentials of both reactants, an important premise for cross cyclo-additions in the cation radical format as outlined by Steckhan.[14] In the presence of tris(*p*-tolyl)aminium salts (ET1) (Chart I) only the DA products and no vinylcyclobutanones were formed (eq 4).
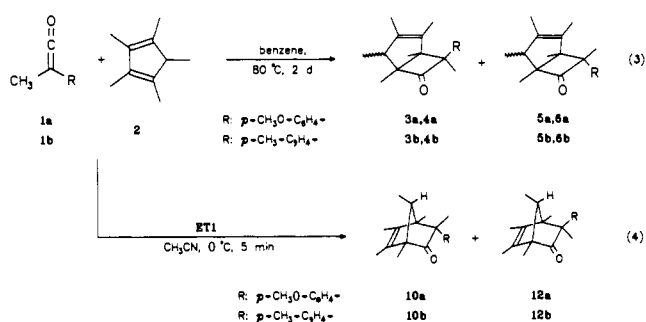
In contrast, the thermal reaction of **1** and **2** proceeded as antic-ipated, yielding exclusively the vinylcyclobutanones (eq 3). Hence, this example constitutes the first case where the *formal* perise-lectivity of the ketene/diene format could be controlled by electron transfer.

Most importantly, cation radical catalysis has additionally proven to be a powerful tool for accelerating Woodward–Hoff-mann-forbidden processes, e.g., [1,3] sigmatropic rearrangements. Thus, both vinylcyclopropanes[15] and vinylcyclobutanes[16] could be smoothly rearranged in the presence of one-electron oxidants to cyclopentenes and cyclohexenes, respectively, as demonstrated recently by Dinnocenzo and Bauld independently. In continuation
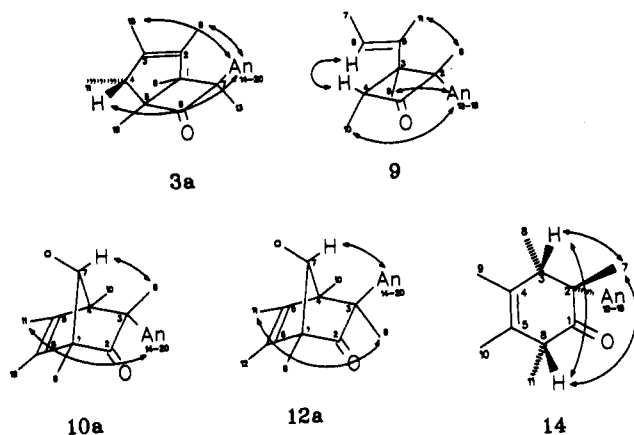
of their work, we have developed a second, albeit indirect, approach to ketene/diene DA products (e.g., **10**, **12**) (Chart II) that is based on the cation radical catalyzed [1,3] sigmatropic rearrangement of vinylcyclobutanones (e.g., **3–6**). In contrast to the cation radical DA reaction, this strategy should also allow unstable ketenes to react via their stable vinylcyclobutanones. Because the vinyl-cyclobutanone rearrangement gives only negligible yields under photochemical or thermal conditions,[17] the cation radical rear-rangement constitutes an important novel approach to the formal [4 + 2] products of ketenes and dienes. The mechanism and the stereochemical results of this rearrangement will be discussed in detail in this paper. In addition, a comprehensive mechanistic study of the aminium salt initiated DA reaction of ketenes with dienes is described in order to assess the scope of this new reaction mode.

Model Compounds and Products

Vinylcyclobutanones: Synthesis. A mixture of vinylcyclo-butanones was obtained from the thermal reaction of ketenes **1a,b** and diene **2** after 2 days in benzene at reflux temperature in yields of 54% (**3a–6a**) and 37% (**3b–6b**) (eq 5). These moderate yields
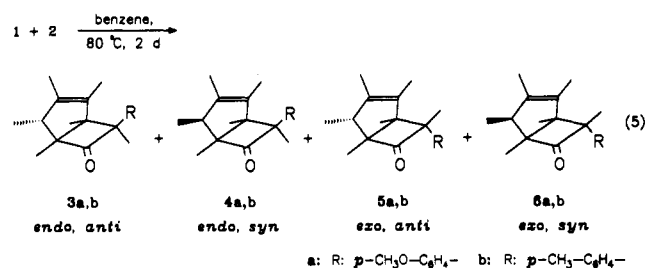
could not be improved in spite of our applying various reaction conditions. The sluggishness of the reaction can be rationalized in terms of the FMO theory,[18] because both the diene ($E_p = 0.87$ V)[19] and the ketenes **1a** ($E_p = 0.91$ V) and **1b** ($E_p = 1.11$ V) exhibit similarly low oxidation potentials in acetonitrile, indicating a large HOMO (diene)–LUMO (ketene) gap. In line with cy-cloadditions of similar systems,[4] the reaction proved to be highly periselective (only [2 + 2] products) and regioselective (only bicyclo[3.2.0]hept-2-en-6-ones and no bicyclo[3.2.0]hept-2-en-7-ones). The endo isomers were formed preferentially with endo/exo ratios of 53:1 (**3a,4a:5a,6a**) and 27:10 (**3b,4b:5b,6b**), respectively. While endo and exo isomers could be separated after elaborative reversed-phase HPLC, we were unable to resolve the

(10) (a) Schutte, R.; Freeman, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3715. (b) Penner, T. L.; Whitten, D. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1970**, *92*, 2861. (c) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (d) Libman, J. *J. Chem. Soc., Chem. Commun.* **1976**, 361. (e) Mizuno, K.; Kaji, R.; Okada, H.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 594.

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(12) (a) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. (b) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665. (c) Bellville, D. J.; Bauld, N. L.; Pabon, R.; Gardner, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 3584. (d) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 5158.

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(16) Reynolds, D. W.; Harirchian, B.; Chiou, H.-S.; Marsh, B. K.; Bauld, N. L. *J. Phys. Org. Chem.* **1989**, *2*, 57.

(17) (a) Jones, G., II; Zalk, S. A. *Tetrahedron Lett.* **1973**, 4095. (b) Hostettler, H. U. *Tetrahedron Lett.* **1965**, 687.

(18) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1982.
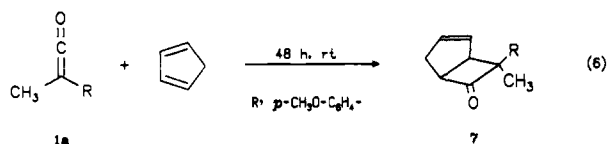
(19) All oxidation potentials are referenced to the saturated calomel electrode (SCE).

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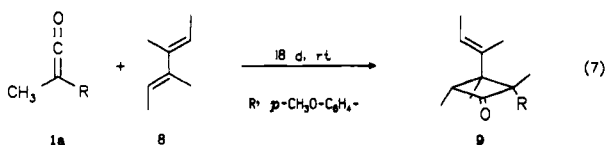syn and anti isomers. In all cases, the anti isomers were formed predominantly.

Vinylcyclobutanones: Structural Assignment. All vinylcyclobutanones show ν_{CO} = 1763–1769 cm^{-1} and ^{13}C NMR shifts of 215–224 ppm, both indicative of four-membered-ring ketones. The mass spectra display strong signals derived from a [2 + 2] cycloreversion. The stereochemical assignment is made mostly on the basis of ^{1}H NMR shifts and ^{1}H NMR difference NOE spectra. The most important NOE enhancements of two of the vinylcyclobutanones (**3a** and **9**) for the structure assignment are depicted in Figure 1.

Correct assignment of the structures of **3–6** is critical for the stereochemical analysis of the aminium salt initiated rearrangement, and the main arguments will therefore be discussed in detail. Characteristic for **3a** are strong NOE enhancements between the aryl protons, on one hand, and methyl groups 9-H and 10-H and proton 4-H, on the other, proposing that the anisyl group is endo and methyl group 11-H is anti. This is corroborated by a negative NOE effect between the aryl protons and 11-H. The assignment of **4a** as an endo, syn vinylcyclobutanone is straightforward, since **4a** and **3a** exhibit almost identical ^{1}H NMR spectra except for the CHCH$_3$ group. In the ^{1}H NMR[20] of **4a** proton 4-H shows an upfield shift ($\Delta\delta$ = –0.38 ppm) and methyl group 11-H a downfield shift ($\Delta\delta$ = +0.31 ppm) compared to **3a**. In contrast, isomers **5a** and **6a** exhibit a characteristic upfield shift for the methyl protons 8-H and 12-H, indicative of an exo structure.[20] This assignment is supported by a downfield shift for the aryl protons in **5a,6a** relative to **3a,4a**, since they are removed from the shielding zone of the C=C bond. Again, the relative shifts of the CHCH$_3$ group are used to assign to **5a** an exo, anti configuration and to **6a** an exo, syn configuration. The proton NMR spectra of **3b–6b** are identical to those of **3a–6a** to within 0.02 ppm (except for the aryl and *p*-methyl protons); thus the stereochemistry of **3b–6b** was established in analogy to **3a–6a**.

A single stereoisomer was isolated in 75% yield from the thermal reaction of **1a** with an excess of cyclopentadiene after 48 h at room temperature (eq 6). In line with ^{1}H NMR data of similar systems in the literature,[21] an endo structure was assigned to vinylcyclobutanone **7**.

upfield shift of methyl group 9-H induced by the anisyl group. The vinyl group is located above the plane of the cyclobutanone ring, as indicated by NOE enhancements between protons 6-H and 4-H on one side and negative NOE effects between protons 7-H and 4-H on the other.

Diels–Alder Adducts. Norbornenones **10–12** (Chart II) were isolated from cation radical initiated reactions, since their independent synthesis via a triplex DA reaction[22] of 2-(*p*-anisyl)-1-

Chart II
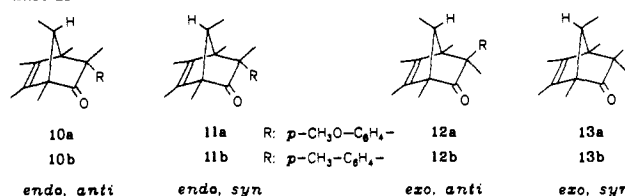
methoxy-1-(trimethylsiloxy)propene with pentamethylcyclopentadiene in the presence of 9,10-dicyanoanthracene failed to work. Compounds **10** and **12** were obtained from cation radical initiated cycloadditions[13] (eq 4) and separated after liquid chromatography and additional reversed-phase HPLC. From the cation radical initiated rearrangements **10/11** and **12** were isolated, but the anti and syn isomers (**10** and **11**) could not be separated. All isomers show ν_{CO} = 1733–1734 cm^{-1} as well as mass fragmentation patterns and NMR spectra that are consistent with the proposed norborn-5-en-2-one structure. The stereochemical assignments were based on the characteristic aryl shift effects on neighboring methyl groups and ^{1}H NMR difference NOE spectra.

The assignment of **10a** as an endo isomer with an anti methyl group is based on NOE effects between (1) the aryl protons and the methyl protons 11-H and (2) proton 7-H and methyl group 9-H (Figure 1). In addition **10a** shows a characteristic high-field shift (δ = 0.76 ppm) for the 11-H methyl group, which can be rationalized by the presence of an endo anisyl group. In contrast, the 12-H methyl group absorbs at δ = 1.54 ppm. The NOE effects and the high-field δ = 0.82 ppm of methyl protons 13-H are indicative of an anti 13-H methyl group in **10a**. An unambiguous assignment of the structure of **10a** was obtained by X-ray analysis that confirmed the above structure proposal.[23]

The proton shifts for the endo, syn isomer **11a** are similar to those of **10a**, except δ(7-H) and δ(13-H) differ from those of **10a** by 0.1 ppm. In contrast, **12a** exhibits the typical spectra of an exo norbornenone with an anti methyl group, mainly on the basis of the NOE effect between methyl groups 9-H and 11-H and the aryl protons and proton 7-H (Figure 1). Both vinylic methyl groups, 11-H and 12-H, do not undergo a high-field shift compared to **10a**. Finally, no exo, syn isomer **13a** could be detected in the aminium salt initiated rearrangement of **3a–6a** or in the DA reaction of **1a** and **2**.

The NMR spectra of the tolyl-substituted norbornenones **10b–12b** closely resembled those of the anisyl analogues **10a–12a**; hence, the stereochemistry was inferred by analogy.

Cyclohexenone **14** was isolated from the cation radical initiated rearrangement of **9** (eq 8). The ν_{CO} of 1710 cm^{-1} and the ^{13}C NMR shift at 214.8 ppm (C=O) are indicative of a cyclohexenone without a conjugated C=C—C=O group. The stereochemistry of **14** was inferred from the NOE effects between protons 3-H and 6-H, on one hand, and methyl group 7-H and protons 3-H, 6-H, on the other.
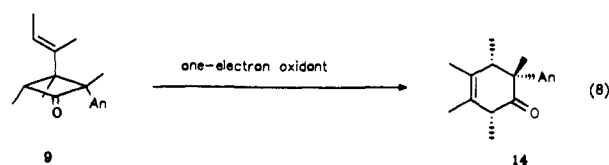
Results and Discussion

Diels–Alder Reaction. The reaction conditions were directly adapted from Bauld's experimental procedures for the cation radical catalyzed cross dimerizations of dienes and olefins,[24] except that acetonitrile as solvent proved to be superior to methylene chloride.

(20) The numbering of the carbon skeleton follows the pattern provided in Figure 1 for vinylcyclobutanone **3a**.

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(23) The X-ray structure was determined at the University of Freiburg X-ray analysis facility by Dr. M. Keller. The complete data can be obtained from the authors upon request.

(24) Reynolds, D. W.; Lorenz, K. T.; Chiou, H.-S.; Bellville, D. J.; Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1987**, *109*, 4960.

Table I. Products of the Cation Radical Initiated Cycloaddition of Ketene **1a** with Diene **2** at 0 °C and of Some Related Control Experiments as Determined by ^{1}H NMR

catalyst	mol %[a]	1a:2 (ratio)	concn[b] (M)	time[c] (min)	products (%)					
					10a	12a	16a	17a	18a	other
ET2	30	(3:1)	1.24	5	24	9	22	20[a]		
ET3	25	(1:1)	0.50	5			25	8		
ET1a	10	(1:1)	0.50	5	7	2	2	34		
ET1a	25	(1:1)	0.50	5	31	11	11	14		
ET1a	50	(1:1)	0.50	15	29	11	9	17		
ET1a	100	(1:1)	0.50	30	30	12	3	14		
ET1a	25	(1:1)	0.10	5	20	6	8	14		
ET1a	25	(1:1)	1.00	5	23	6	3	15		
ET1a	25	(1:1)	0.50	0.5	18	6	4	27		
ET1a	25	(1:1)	0.50	1	16	7	7	27		
ET1a	25	(1:1)	0.50	2	24	20	8	15		
ET1b/ET1r	25/250	(1:1)	0.50	10	21	8	18	9		
CF$_3$SO$_3$H[d]	170	(2.5:1)	0.36	90			45	5		
ET1a/15	50/55	(1:1)	0.50	20	18	5		5		
ET1a/15	50/2.5	(1:1)	0.50	20	21	10	9	27		
AlCl$_3$[d]	100	(1:1)	0.50	5			3		40	dimers of 2
SbCl$_5$[d]	100	(1:1)	0.50	5			9		10	dimers of 2
BF$_3$·Et$_2$O[d]	100	(1:1)	0.50	5			4		40	dimers of 2
ET2	20	2 only	0.31	30						dimers of 2

[a] Mol % in relation to **2**. [b] Concentration of **1a**. [c] Time until the reaction was quenched by addition of a sodium methoxide solution in methanol. [d] Quenched by addition of water.

Table II. Products of the Cation Radical Initiated Cycloaddition of Ketene **1b** with Diene **2** at 0 °C and of Some Related Control Experiments as Determined by ^{1}H NMR

catalyst	mol %[a]	1b:2 (ratio)	concn[b] (M)	time[c] (min)	products (%)				
					10b	12b	16b	17b	other
ET1b	50	(1:1)	0.50	5	14	6	6	17	dimers of 2
ET1b	50	(5:1)[d]	2.50	5	30	9	<2	36	
ET1b	50	(1:5)[e]	0.50	5	5	1	<2	12	dimers of 2
ET1b/15	50/55	(1:1)	0.50	5	13	4		27	
CF$_3$SO$_3$H	150	(1:1)	0.50	5			59	19	
ET1b	50	(5:1)[d]	2.50	5	31	7	<2	120	
ET1b	50	1b only	0.50	5				9	polymers
ET3	50	(1.5:1)[d]	0.75	5	4	1	14	6	
ET1b[f]	50	(5:1)[d]	2.50	5	31	7			

[a] Mol % in relation to **2**. [b] Concentration of **1b**. [c] Time until the reaction was quenched by addition of a sodium methoxide solution in methanol. [d] Yields are related to diene **2**. [e] Yields are related to ketene **1b**. [f] At −10 °C.

Table III. Products of the PET-Induced Cycloaddition as Determined by ^{1}H NMR

catalyst system	mol %[a]	ketene/diene	concn[b] (M)	time	products (%)				
					10	12	17	18	other
ET4/hν[c]	20	1a:2 (5:1)	1.00	3.5 days	5	<2		26[a]	261% 1a[a] 17% 2 8% 30a
DCA/19/hν[d]	10/1000	1a:2 (1:1)	0.29	3 h				74	
ET4/19/hν	20/500	1a:2 (2:1)	0.57	3 h			109[a]		47% 2
ET4/hν	20	1b:2 (5:1)	1.00	24 h	5	2			324% 1b[a] 34% 2
TPP[e]/hν	8	1b:2 (5:1)	1.00	24 h	5	2		58[a]	287% 1b[a] 29% 2

[a] In relation to diene **2**. [b] Concentration of ketene. [c] Wavelength 350–390 nm. [d] DCA = 9,10-dicyanoanthracene; wavelength > 350 nm. [e] TPP = 2,4,6-triphenylpyrylium tetrafluoroborate.

For use as one-electron oxidants we probed the aminium salts ET1 and ET2 as well as the iron(III) phenanthroline hexafluorophosphate compound ET3 (Chart I). ET3 has been shown by Kochi[25] to behave as an outer-sphere oxidant, whereas for the aminium salts inner-sphere processes are quite likely.[26] In general, a solution or a suspension of the one-electron oxidant was added to a solution of the ketene and diene within 2 min. Tables I, II, and III depict our results[27] for the cycloaddition of ketenes **1a/1b** to diene **2** probing the influence of the oxidant, reaction time, concentration, and addition of triarylamines.

Table IV. Electron-Transfer Rates Calculated for the Reduction of **10a**[·+] in Acetonitrile by the Various Reductants, Applying the Marcus Theory

reductant	$\lambda(0)$[a] (kcal/ mol)	ΔG_{ET}°[b] (kcal/ mol)	ΔG_{ET}^{*} (kcal/ mol)	log k_{ET}[c] [log (M^{-1} s^{-1})]
1a	60	−13.6	9.7	3.2
2	60	−14.5	8.6	4.1
ET3r	37	−13.2	7.5	5.0
ET2r	36	−10.1	4.6	7.3
ET1r	36	−17.1	2.5	9.0

[a] Reorganization energy for the heteroexchange reaction between **10a**[·+] and the listed reductants. The value of $\lambda(0)$ has been taken as a mean value of the individual λ_i values of the corresponding self-exchange reactions; see ref 35. [b] The corrected standard free energy change of the electron-transfer step as defined in ref 36. [c] Calculated from the Eyring equation.

(25) (a) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593. (b) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.

(26) Eberson, L.; Shaik, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4484.

(27) The product yields were determined by ^{1}H NMR spectroscopy using *m*-nitroacetophenone as internal standard.

Ketene–Diene [4 + 2] Cycloaddition Products

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$$1 + 2 \xrightarrow[\text{oxidant}]{\text{one-electron}}$$

(9)

| R: p-CH$_3$O-C$_6$H$_4$- | 10a,12a | 18a | 17a | 18a |
| R: p-CH$_3$-C$_6$H$_4$- | 10b,12b | 16b | 17b | 18b |
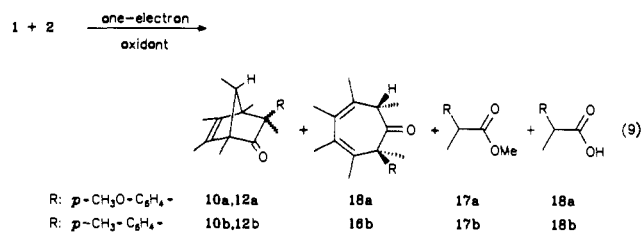
As noted in Table I, the DA reaction could successfully be initiated with oxidants ET1a, ET1b, and ET2. The best yield of DA products **10a,12a** (42%) was obtained at 0 °C in acetonitrile, when a solution of 25 mol % ET1a was added to a 0.5 M solution of both **1a** and **2** within 2 min. The stronger oxidant ET2 also afforded **10a** and **12a** in acceptable amounts at a ketene/diene ratio of 3:1. Increasing the time beyond 5 min until a sodium methoxide solution was added to quench the reaction did not improve the yields. The yield was not significantly affected when higher amounts of the aminium salts were used, when triarylamine was added as reductant, or when the counterion was changed as in ET1b. Importantly, no vinylcyclobutanones **3a–6a** were detected as products.

Using the best conditions for the transformation of **1a** and **2** for the reaction of **1b** and **2** afforded **10b,12b** in only 20% yield. However, the yield was almost doubled by increasing the ketene/diene ratio to 5:1 and decreased to 6% when a ketene/diene ratio of 1:5 was used (Table II). No significant change occurred when the reaction was run at −10 °C.

Diels–Alder Reaction: Mechanistic Aspects. Recently, there has been a major concern that aminium ion salts can initiate Brønsted acid catalyzed reactions.[28] Fortunately, such a mechanism for the formation of the DA products **10** and **12** can definitely be ruled out, since both are equally formed in the presence of a slight excess of di-*tert*-butylpyridine (**15**), albeit in lower yields. In contrast, the cycloheptadienones **16** are formed in an acid-catalyzed process as demonstrated by a control experiment using trifluoromethanesulfonic acid.[29] Since all the aminium salts contain negative counterions, prone to Lewis acid activity,[30] we tested the reactivity of the system **1a/2** in the presence of various Lewis acids. With AlCl$_3$, SbCl$_5$, and BF$_3$·OEt$_2$ no cycloaddition products of **1a** and **2** were found, except for **16a**, which was formed in less than 10% yield. Rather, formation of several dimers and dehydrodimers of **2** was observed.

Interestingly, no DA products from **1a** and **2** were formed with ET3 as oxidant, whereas cycloheptadienone **16a** was detected in 25% yield. In contrast, the reaction of *p*-tolylmethylketene (**1b**) with **2** in the presence of ET3 afforded 5% **10b,12b**, although here again, cycloheptadienone **16b** (14%) constituted the major non-polymeric product. Similarly, the cycloaddition of **1a,b/2** under photoinduced electron-transfer (PET) conditions[31] afforded the DA products only in very low yields (Table III). While PET initiation, which has rarely been applied in cross cycloadditions,[32] is apparently not an efficient method to obtain the ketene/diene DA products, the results propose that cation radicals are important as intermediates.

$$1 + 2 \xrightarrow{\text{PET}} 10 + 12 + 17 + 18 \qquad (10)$$
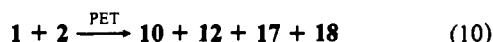
Diels–Alder Reaction: Cation Radical Intermediates versus Aminium Salt Complexes. Why does initiation with the iron(III) salt ET3 ($E_{1/2}$ = 1.09 V),[25] in contrast to aminium ion salt initiation, give no DA products starting from **1a** and **2** and only

negligible amounts from **1b** and **2**? Obviously, the oxidation strength does not seem to be the decisive factor because both aminium ion salts, ET1 ($E_{1/2}$ = 0.76 V)[33] and ET2 ($E_{1/2}$ = 1.06 V),[33] although they display a $\Delta E_{1/2}$ = 0.3 V, trigger the DA reaction equally well. This immediately raises the question of whether true cation radical intermediates or aminium salt complexes are involved.

From Eberson's recent study of the ET2-initiated DA dimerization of cyclohexa-1,3-diene (CHD) it is most likely that the dimer cation radical ($E_{1/2}$ = 2.17 V) is reduced by tris(*p*-bromophenyl)amine (ET2r) (Chart I) and not by the diene.[34] This was deduced from the calculated electron-transfer rates, which reflect the much lower oxidation potential of ET2r ($E_{1/2}$ = 1.06 V) than of CHD ($E_{1/2}$ = 1.66 V) and the high reorganization energy of CHD. Hence, the DA reaction of CHD in the presence of aminium ion salts follows a conventional catalytic mechanism rather than a pure cation radical chain mechanism (eqs 11–13).

$$CHD + NR_3^{\cdot+} \rightarrow CHD^{\cdot+} + NR_3 \qquad (11)$$

$$CHD^{\cdot+} + CHD \rightarrow (CHD)_2^{\cdot+} \qquad (12)$$

$$(CHD)_2^{\cdot+} + NR_3 \rightarrow (CHD)_2 + NR_3^{\cdot+} \qquad (13)$$
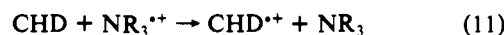
In our system both ketene **1a** (E_p = 0.91 V) and diene **2** (E_p = 0.87 V) exhibit low oxidation potentials, comparable to those of the triarylamines ET1r and ET2r or the iron(II) salt ET3r (Chart I). Therefore, in principle, reduction of **10a**$^{\cdot+}$ (E_p^{red} = 1.50 V) or **12a**$^{\cdot+}$ (E_p^{red} = 1.50 V) can be accomplished either by the reduced form of the one-electron oxidant or by **1a** or **2**. A calculation of the electron-transfer rates[35,36] to **10a**$^{\cdot+}$ from all the possible reductants by applying the Marcus theory[37] provides a simple explanation for the failure of ET3 to effect the cycloaddition (Table IV).

Since the DA product cation radical constitutes a highly unstable entity, fast reduction will be a pivotal element of the reaction sequence. According to the rate estimates in Table IV, the reduction of **10a**$^{\cdot+}$ is most effectively performed by the triarylamines. The iron(II) salt ET3r is a much slower reducing agent because of its double positive charge, and **1a** and **2** are even less effective as reductants because of their high reorganization energies.[36] Thus, it is conceivable that with these reductants electron transfer to **10a**$^{\cdot+}$ cannot compete with other reactions, e.g., deprotonation. This reasoning can also rationalize the result of the **1b/2** cycloaddition. Since the DA product cation radicals **10b**$^{\cdot+}$/**12b**$^{\cdot+}$ (E_p(10b) = 1.56 V) are more readily reduced than **10a**$^{\cdot+}$ or **12a**$^{\cdot+}$, formation of the desired DA products, albeit in low yield, is even possible with ET3r.

Although the presented explanations do not rigorously disprove the involvement of an aminium salt complex, we presume on the basis of Occam's razor for the following discussion that the observed DA reaction proceeds via intermediate cation radicals.

Diels–Alder Reaction: [3 + 2] versus [4 + 1] Mechanism. The question of a [3 + 2] or a [4 + 1] mechanism has been the subject of an ongoing controversy over the last decade for many cation radical catalyzed cycloadditions. A [4 + 1] mechanism has been favored for a long time, since, in contrast to the [3 + 2] version,

(28) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085, 7993.
(29) von Seggern, H.; Schmittel, M. Manuscript in preparation.
(30) The SbCl$_6$⁻ counterion is also known to constitute a weak two-electron oxidant: Cowell, G. W.; Ledwith, A.; White, A. C.; Woods, H. J. *J. Chem. Soc. B* **1970**, 227.
(31) Chanon, M.; Eberson, L. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Chapter 1.11.
(32) (a) Mlcoch, J.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 412. (b) Laszlo, P.; Lucchetti, J. *Tetrahedron Lett.* **1984**, *25*, 1567. (c) Gieseler, A.; Steckhan, E.; Wiest, O. *Synlett* **1990**, 275.

(33) Steckhan, E. *Top. Curr. Chem.* **1987**, *142*, 1.
(34) Eberson, L.; Olofsson, B. *Acta Chem. Scand.* **1991**, *45*, 316.
(35) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer Verlag: Berlin, 1987.
(36) The reorganization energies (λ_i, kcal mol⁻¹) of the individual redox pairs have been approximated by following the guidelines given in refs 34 and 35: λ(**1a**$^{\cdot+}$/**1a**) = 60, λ(**2**$^{\cdot+}$/**2**) = 60, λ_i(ET1/ET1r) = λ_i(ET2/ET2r) = 12, and λ_i(ET3/ET3r) = 14.
(37) According to an analysis by Eberson and Shaik,[26] outer-sphere oxidations are rare cases in electron-transfer reactions, one prominent example being the oxidation of tetraalkylstannanes by ET3.[25] Thus, we have to take into account that inner-sphere processes may be operative for the reduction of **10a**$^{\cdot+}$ by the triarylamines, ketenes **1**, and diene **2**. Nevertheless, as an approximation we have calculated the electron-transfer rates[35,36] by applying the Marcus theory, which is in principle only applicable to outer-sphere electron-transfer reactions: Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

it is formally symmetry allowed[38] and virtually all of the earlier cation radical DA cross reactions involved readily oxidizable dienophiles.[11] Only recently, the elegant studies by Steckhan[14] and Bauld[39] have shown that the [3 + 2] pathway is a viable mechanistic alternative, if the diene prefers the s-cis conformation. From our results, the cation radical initiated ketene/diene cycloaddition most likely follows the [3 + 2] pathway (eqs 14–16) and not the [4 + 1] pathway (eqs 17–19).

[3 + 2] mechanism:

$$\text{diene} - e^- \rightarrow \text{diene}^{\bullet+} \tag{14}$$

$$\text{diene}^{\bullet+} + \text{ketene} \rightarrow \text{DA}^{\bullet+} \tag{15}$$

$$\text{DA}^{\bullet+} + \text{diene (or ET1r)} \rightarrow \text{DA} + \text{diene}^{\bullet+} \text{ (orET1)} \tag{16}$$
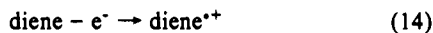
DA: Diels–Alder product

[4 + 1] mechanism:

$$\text{ketene} - e^- \rightarrow \text{ketene}^{\bullet+} \tag{17}$$

$$\text{ketene}^{\bullet+} + \text{diene} \rightarrow \text{DA}^{\bullet+} \tag{18}$$

$$\text{DA}^{\bullet+} + \text{ketene (or ET1r)} \rightarrow \text{DA} + \text{ketene}^{\bullet+} \text{ (or ET1)} \tag{19}$$
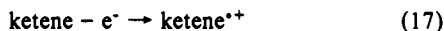
Since 1a and 2 exhibit similar oxidation potentials, this conclusion is primarily based on the experimental results of the cycloaddition of 1b (E_p = 1.11 V) with 2 (E_p = 0.87 V). When ET1 is used as oxidant, 2 is much more readily oxidized than 1b, as demonstrated by a simple test. Thus, addition of 1b to a solution of ET1 in acetonitrile, under the cycloaddition conditions, did not decolorize the blue solution. In contrast, in the reaction of ET1 with 2 the blue aminium ion salt color was immediately lost, and formation of dimers and dehydrodimers of 2 was registered.[40] While this observation does not necessarily disprove the [4 + 1] mechanism, the [3 + 2] pathway is substantiated by the higher yields of DA products with increasing ketene 1b/diene 2 ratios (Table II), since trapping of the diene cation radical with a ketene to yield the DA$^{\bullet+}$ is accelerated.[41] On the other hand, an excess of diene (1b:2 = 1:5) almost exclusively leads to 2-derived dimers and only small amounts of DA products. In light of these results, the ketene cation radicals tend to deprotonate rather than to cycloadd. Fast-scan cyclic voltammetry (cv) studies (v = 10⁵ V/s), exhibiting irreversible waves, and stoichiometric oxidation studies on our model ketenes propose that 1a$^{\bullet+}$ and 1b$^{\bullet+}$ deprotonate rapidly in the methyl group, since products like ArC(=CH₂)C-OOCH₃ and ArCH(CH₂OCH₃)COOH could be detected in the presence of methanol.

Altogether, the required high amounts of aminium salt point to a rather short chain length in the cycloaddition of 1 and 2. The extremely high consumption of oxidant is ascribed to formation of easily oxidizable products presumably formed via deprotonation of intermediate cation radicals, as indicated by the significant quantity of 16 and of polymers formed.

Diels–Alder Reaction; Stereochemistry and Scope. The observed endo selectivity is moderate but in agreement with results of other cation radical catalyzed cycloadditions.[11] More surprising is the high facioselectivity of the DA reaction with only the anti norbornenones 10 and 12 formed. Since 11 is stable to the reaction conditions, the observed facioselectivity is indeed a direct consequence of selectivity in the cycloaddition step.[42] This stereochemical preference can tentatively be rationalized on the basis

of thermochemical data, assuming that this stability order is translated equally into the transition-state energies. As indicated by our AM1 calculations[43] on the four isomeric norbornenone cation radicals, formation of the anti isomer 10a$^{\bullet+}$ (ΔH_f = 163.0 kcal/mol) is favored over syn isomer 11a$^{\bullet+}$ (ΔH_f = 165.1 kcal/mol) for the endo compounds, while for the exo isomers *anti*-12a$^{\bullet+}$ (ΔH_f = 167.4 kcal/mol) is more stable than *syn*-13a$^{\bullet+}$ (ΔH_f = 170.3 kcal/mol).[44]

A severe drawback to a general use of the cation radical catalyzed ketene/diene cycloaddition is the necessity of starting from stable ketenes. Moreover, the oxidation potentials of both components need to be close; otherwise, the intermediate DA$^{\bullet+}$ are too high in energy to be accessible in the cycloaddition step. Hence, no DA products of ketene 1a with dienes like 8 (E_p = 1.69 V), cyclopentadiene, or 2,3-dimethylbutadiene (E_p = 1.95 V) were observed. More promising is the reaction of 2 with other ketenes, e.g., diphenylketene and bis(4-tolyl)ketene, since ketene/diene adducts (≈10%) could be detected by GC/MS, although formation of dimers derived from the diene constituted the major pathway.[45] Further work to accrue a corpus of knowledge in this direction is warranted.

In summary, the cation radical catalyzed DA reaction complements ideally the thermal chemistry of ketenes. For the first time it proved possible to control the formal periselectivity of ketene/diene cycloadditions by using either thermal conditions or the cation radical format. However, the cation radical route seems to be of somewhat limited scope. To further probe the viability of this concept, the reactions of stable ketenes, e.g., diarylketenes, with selected dienes will be studied in more detail in the near future.

Vinylcyclobutanone Rearrangement. As demonstrated by Bauld and co-workers in important papers recently, cation radical catalyzed formal DA reactions may proceed in a stepwise fashion via a cyclobutanation that is followed by a vinylcyclobutane rearrangement.[16,46] Both processes are cation radical catalyzed reactions in the formal DA cycloaddition of phenyl vinyl sulfide and 1,1'-bicyclopentenyl. Most importantly, the vinylcyclobutane rearrangement in the presence of one-electron oxidants constitutes a valuable preparative route, since a formally symmetry forbidden process can be accomplished with astounding ease. The rearrangement was reported to proceed stereospecifically with retention of configuration at the migrating center[16] (eq 20), and this was

$$\text{R: } p\text{-CH}_3\text{O-C}_6\text{H}_4\text{--}$$
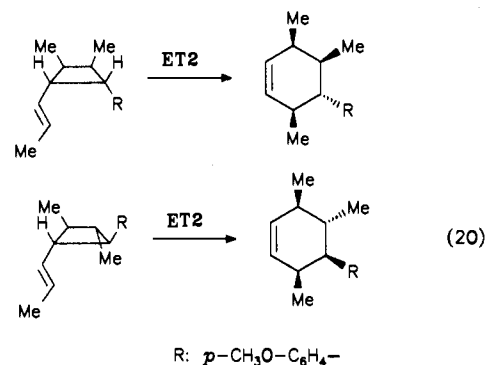
rationalized by assuming a concerted suprafacial rearrangement. Indeed, ab initio calculations on the cation radical rearrangement of the parent vinylcyclobutane revealed a concerted s,r reaction path (suprafacial/retention) with an activation barrier of 9.4 kcal/mol.[47] At the same time, Dinnocenzo and Conlon reported several cation radical catalyzed vinylcyclopropane–cyclopentene rearrangements and showed that the rearrangement took place

(38) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(39) Chockalingam, K.; Pinto, M.; Bauld, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 447.

(40) The dimers and dehydrodimers of 2 could be identified by GC/MS. While some of them are formed by acid-catalyzed processes, others presumably are the result of cation radical catalyzed cycloadditions. The cation radical of 2 has recently been characterized: Courtneidge, J. L.; Davies, A. G.; Shields, C. J.; Yazdi, S. N. *J. Chem. Soc., Perkin Trans. 2* **1988**, 799.

(41) The alternative hypothesis that increasing the amount of ketene solely helps to reduce the yield of DA$^{\bullet+}$ can easily be ruled out on the basis of the calculated electron-transfer rates as demonstrated in Table IV.

(42) An anti:syn facioselectivity of 91:9 has been found in the thermal DA reaction of 2 and dimethyl maleate: Burnell, D. J.; Valenta. Z. *J. Chem. Soc., Chem. Commun.* **1985**, 1247.

(43) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(44) According to MM2-86 force field calculations,[7] the stability order of the neutral norbornenones 10a–13a is different, although the thermochemical preference for the anti isomers is preserved. Final steric energies (kcal mol⁻¹) are in parentheses: 10a (34.23) vs 11a (36.81) and 12a (33.65) vs 13a (37.08).

(45) von Seggern, H.; Schmittel, M. Unpublished results.

(46) Kim, T.; Pye, R. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 6285.

(47) Bauld, N. L. *J. Comput. Chem.* **1990**, *11*, 896.

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Table V. Products of the Cation Radical Initiated Vinylcyclobutanone Rearrangement and of Related Control Experiments as Determined by ^{1}H NMR

catalyst (mol %)	reactants	time^a (min)	ϑ (°C)	products (%)				
				10	11	12	20	other
ET1b (25)	3a,4a (85:15)	4	0				50	
ET2/15 (50/55)	3a,4a (92:8)	2	65	54	<2	15		
ET2/15 (50/55)	3a,4a (92:8)	4	40	43	4	10		
ET2/15 (40/55)	3a,4a (92:8)	2	0	38	6	7		13% 3a
ET2/15 (10/11)	3a,4a (92:8)	5	0	32	<1	6		11% 3a
ET2/15 (50/55)	3a,4a (92:8)	45	−20	51	9	7		
ET2/15 (50/55)	3a,4a (85:15)	5	0	73^b	13^b	14^b		
ET2/15 (50/55)	5a,6a (73:27)	5	0	16^b	18^b	66^b		
ET4/19 (20/100)	3a,4a (92:8)	2 h^c	rt^d	20		9		
ET2/15 (50/55)	10a	5	0	69		5		
ET2/15 (50/55)	12a	5	0	4		35		
ET2/15 (50/55)	10a,12a (32:68)	5	0	26		31		
ET2/15 (50/55)	3b,4b (91:9)	2	37	34		9		
ET2/15 (50/55)	3b,4b (91:9)	2	52	39		10		
ET2(50)	3b,4b (91:9)	5	0				24	
ET4/19 (20/680)	3b,4b (85:15)	3.5 h^c	rt^d	20		10		17% 3b
DCB^e/19 (20/1000)	3b,4b (85:15)	5 h^c	rt^d	10		5		21% 3b
ET4/LP^f (20/1300)	3b,4b (85:15)	9 h^c	rt^d	12		12		10% 3b

^{a}Time in minutes unless noted differently. ^{b}Yields normalized to 100%. ^{c}Time of irradiation. ^{d}Room temperature. ^{e}DCB: 1,4-dicyanobenzene. ^{f}LP: lithium perchlorate.

with total loss of stereochemistry via an open trimethylene cation radical (eq 21).[15,48]

(21)

6 : 1

R: p-CH$_3$O–C$_6$H$_4$–
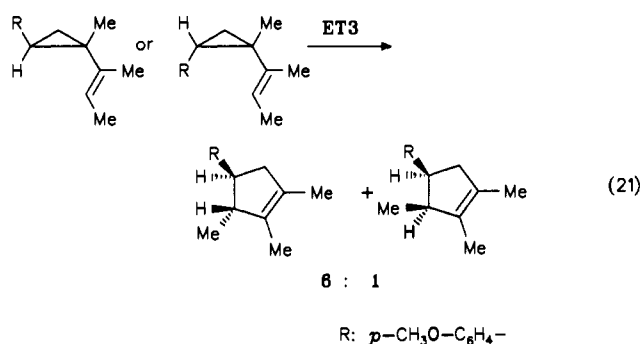
In order to probe whether vinylcyclobutanones could also be rearranged by a cation radical route, we first reacted 3a,4a with ET1b (25 mol %) as oxidant under exactly the same conditions as applied for the cycloaddition. However, only an undesired acid-catalyzed rearrangement to the tetralinone 20a was observed,[29] a reaction type that has earlier been described by Lee-

(22)

3a,4a   20a
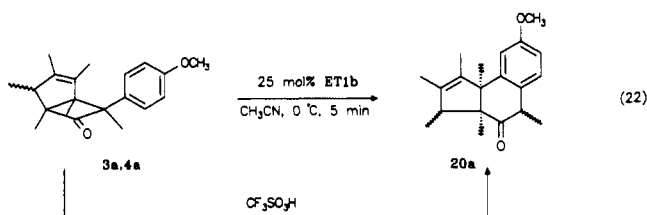
Ruff.[49] Obviously, some of the intermediate cation radicals undergo deprotonation, thus triggering acid-catalyzed processes.

Therefore, it proved indispensable to add a slight excess (relative to the oxidant) of di-tert-butylpyridine (15) in order to prevent acid-catalyzed side reactions. Nevertheless, even in the presence of ET1b (25 mol %) and base only the starting material was recovered from the anticipated rearrangement of 3a–6a to [4 + 2] products, presumably because of the high oxidation potentials of 3a,4a (E_p = 1.55 V) and 5a,6a (E_p = 1.55 V). While this illustrated convincingly that vinylcyclobutanones are not inter-

(48) Dinnocenzo, J. P.; Conlon, D. A. Quoted in: Boche, G.; Walborsky, H. M. Cyclopropane Derived Reactive Intermediates; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1990; Chapter 5.
(49) (a) Lee-Ruff, E.; Hopkinson, A. C.; Dao, L. H. Can. J. Chem. 1981, 59, 1675. (b) Abegg, V. P.; Hopkinson, A. C.; Lee-Ruff, E. Can. J. Chem. 1978, 56, 99. (c) Dao, L. H.; Hopkinson, A. C.; Lee-Ruff, E. Tetrahedron Lett. 1978, 1413.

mediates in the aforementioned DA reaction, it suggested the use of stronger oxidants. Indeed, when we applied aminium salt ET2, the rearrangement of 3a–6a to 10a–12a proceeded in less than 5 min to completion at 0 °C (eq 23).

(23)

3 6   10 ... 12

R: p-CH$_3$O–C$_6$H$_4$– or p-CH$_3$–C$_6$H$_4$–
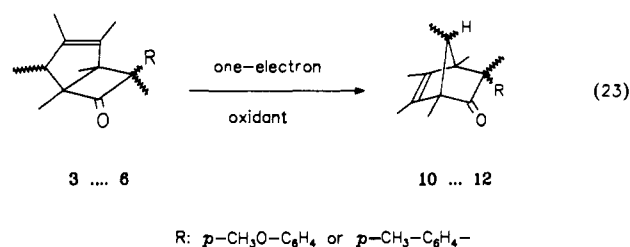
Although in general high amounts of the aminium salt had to be used, 10 mol % of ET2 formed up to 38% of the rearrangement products 10a–12a (Table V), thus pointing to a chain reaction. Higher yields (71%) were obtained when 50 mol % of oxidant was used at elevated temperature, i.e., 65 °C. Again, similar to the findings with the DA reaction, the iron(III) salt ET3 did not work to rearrange 3a,4a, and only the starting material was recovered. On the other hand, this time the rearrangement worked out nicely under PET conditions, albeit the yields were still much lower than with aminium salt initiation.

In spite of their higher oxidation potentials, 3b,4b (E_p = 1.76 V) could also be rearranged to the norbornenones using oxidant ET2, but at slightly higher temperatures (Table V). Since isolation of 5b,6b had proven to be extremely elaborative, no rearrangement experiments with them were undertaken.

Vinylcyclobutanone Rearrangement: Mechanism. Due to the fact that the vinylcyclobutanone rearrangement could be initiated by both aminium salts and various PET systems, we assume in analogy to other systems in the literature that cation radicals are the crucial intermediates. The failure to rearrange the vinylcyclobutanones using ET3 can be ascribed to the slow reduction of the DA$^{•+}$ by ET3r as noted above for the DA reaction.

Formally two plausible possibilities exist to rearrange a vinylcyclobutanone, e.g., 3a$^{•+}$ (Figure 2). Either bond 1 is cleaved or both bonds 1 and 2 are broken.

The latter hypothesis can easily be discarded, since upon dissociation into a ketene and diene cation radical an identical endo/exo product ratio should be obtained for both the endo and exo isomeric vinylcyclobutanones as well as for the DA reaction. In addition, it is known from the aminium salt initiated DA reaction that only anti norbornenones are formed, while in the rearrangement of 3a–6a syn isomer 11a is also detected. We therefore presume that bond 1 is selectively cleaved in the course of the reaction.

Figure 2. Two mechanistic possibilities of bond cleavage for the cation radical rearrangement of **3a** to **10a** and **12a**.

It seemed important to probe whether acyclic dienes could also be used in this two-step approach to [4 + 2] products. Thus, vinylcyclobutanone **9** (E_p = 1.41 V) was reacted with ET2 (50 mol %) in the presence of di-*tert*-butylpyridine (**15**) (55 mol %), and after a clean reaction it gave the desired product **14** (85%; isolated yield: 65%). The rearrangement could also be effected using PET conditions (20 mol % ET4 and 1000 mol % **19**) in 56% yield.[27]

(24)
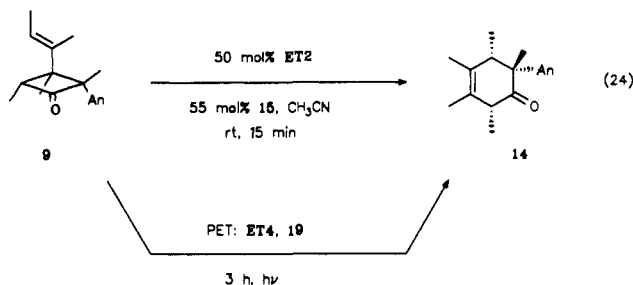
While acid catalysis[29] can rigorously be excluded for the rearrangement of **3–6** to **10–12**, this is not necessarily true for the reaction of **9** to **14**. Indeed, when **9** was reacted with 150 mol % of trifluoromethanesulfonic acid, cyclohexenone **21** was formed in 48% yield (eq 25), presumably via an acid-catalyzed process

(25)
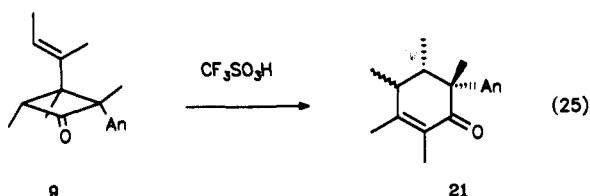
involving **14** as intermediate. Nevertheless, in the aminium salt initiated rearrangement of **9** to **14** (eq 24) an acid-catalyzed mechanism is not operative, because the reaction of **9** with the strongest possible acid, di-*tert*-butylpyridinium hexachloroantimonate, afforded the starting material in 95% yield.

Vinylcyclobutanone Rearrangement: Stereochemical Results.
The rearrangement exhibited a surprising stereochemical outcome (Table V). Starting from the endo vinylcyclobutanones **3a,4a** (anti:syn ratio = 85:15), the endo norbornenones **10a,11a** were formed predominantly (**10a,11a:12a** = 86:14). Similarly, starting from the exo vinylcyclobutanones **5a,6a** (anti:syn ratio = 73:27) formation of the exo norbornenone **12a** was favored (**10a,11a:12a** = 34:66).

For a better understanding of these stereochemical results, we analyze separately the rearrangement of all four vinylcyclobutanones **3a–6a**. Assuming that during the aminium salt initiated rearrangement no change in the stereochemistry at the CHCH$_3$ group should occur, we can determine the individual rearrangement products of all vinylcyclobutanones at 0 °C. The yields have

Table VI. Temperature Dependence of the Endo:Exo Ratio in the Vinylcyclobutanone Rearrangement of **3a**

T (°C)	ratio **10a:12a**	n^a
65	3.30 ± 0.42	2
40	4.72 ± 0.66	4
0	4.77 ± 0.58	5
−20	6.45 ± 0.59	4

^{a} Number of data points.

Table VII. Time Dependence of the Reactant and Product Ratios in the Aminium Salt Initiated Rearrangement of **3a,4a** (83:17) at 0 °C^a

time^b (min)	**3a**	**4a**	**10a** (%)^c	**11a**	**12a**
0.17	57	14	4		<1
0.33	32	7	35	7	8
0.66	24	?^{d}	39	9	9
1.33	9	?^{d}	49	9	11

^{a} ET2:15 (50:110 mol %) in relation to **3a,4a**. ^{b} Time until the reaction was quenched by addition of a sodium methoxide/methanol solution. ^{c} Relative yields as determined by ¹H NMR. No **5a,6a** or **13a** was detected in the product mixture. ^{d} Less than 2%.

been normalized to 100% for the following analysis (Figure 3). Most interestingly, in the cation radical rearrangement of the four isomeric vinylcyclobutanones **3a–6a** *the whole range from 100% retention to 100% inversion* is observed.

To shed light on the different stereochemical courses of the four closely related systems **3a–6a**, we undertook a series of mechanistic control experiments. Treatment of norbornenones **10a,12a** with the aminium salt ET2 showed them to be configurationally unstable under the conditions applied above (Table V). Thus, endo norbornenone **10a** isomerized to a 93:7 mixture of **10a/12a** after 5 min, while the exo isomer **12a** stereomutated to a 90:10 mixture of **12a/10a**. Since the isomerization was accompanied by a severe decomposition of the starting material, we were not able to determine the equilibrium position. In contrast, the vinylcyclobutanones proved to be configurationally stable: When the pure endo isomer **3a,4a** was subjected to the above reaction conditions for 10, 20, 40, or 80 s, no detectable isomerization to **5a,6a** was observed.[50] A study of the time dependence of the rearrangement of **3a,4a** after 10, 20, 40, 80, and 300 s revealed that the endo:exo ratio **10a,11a:12a** remained constant at 85:15. Thus interconversion of the norbornenones does not play an important role in the DA reaction.

How can we understand the surprising stereochemical outcome in the rearrangement of **3a–6a**? Certainly no frontier orbital controlled reaction as predicted by Dunkin[51] is operative, since both **4a** (inversion) and **6a** (retention) rearrange to the same norbornenone, **11a**. Compound **13a** is not observed. As a consequence, the rearrangement is supposed to proceed via an open distonic cation radical (Figure 2, as in route a), and the stereochemistry is dictated by the much higher energy of **13a**$^{\bullet+}$ (170.3 kcal/mol) vs **11a**$^{\bullet+}$ (165.1 kcal/mol).[43]

But why does rearrangement of both **3a** and **5a** occur with *predominant inversion of configuration*? This stereochemical outcome is reminiscent of various biradical rearrangements such as nitrogen loss from 2,3-diazabicyclo[2.2.1]hept-2-ene,[52] rearrangement of bicyclo[2.1.1]hexene derivatives,[53] and others.[54] According to a recent theory by Carpenter (conservation of

(50) The fact that stereomutation of **3a**$^{\bullet+}$,**4a**$^{\bullet+}$ cannot compete with rearrangement may be rationalized by the results of a recent study on the gas-phase chemistry of the parent cyclobutanone cation radical.[50a,b] Accordingly, in the cation radical an open 1-oxotetramethylene is preferred over a closed cyclobutanone structure, contrary to an earlier proposal by Gross.[50c] (a) Heinrich, N.; Koch, W.; Morrow, J. C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 6332. (b) Stirk, K. G.; Kenttämaa, H. 1. *J. Am. Chem. Soc.* **1991**, *113*, 5880. (c) Dass, C.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 5775.

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(52) (a) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1. (b) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695.

(53) Newman-Evans, R. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 7994.

(54) Borden, W. T.; Lee, J. G.; Young, S. D. *J. Am. Chem. Soc.* **1980**, *102*, 4841.

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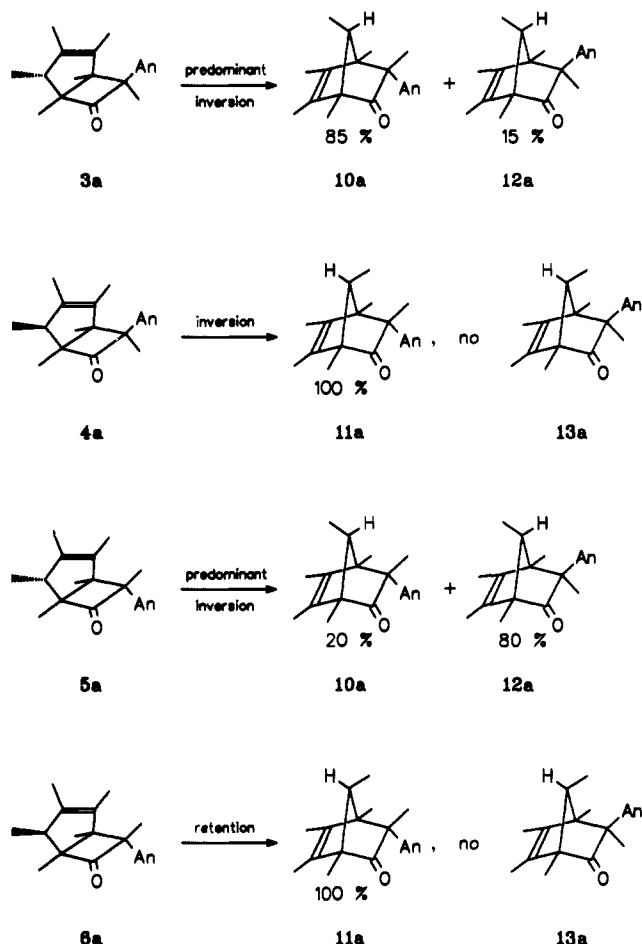
Figure 3. Stereochemical analysis of the vinylcyclobutanone rearrangement assuming that no loss of stereochemistry about the CHCH₃ group should occur. All yields are normalized to 100%.

Figure 4. Proposed mechanism for the dominant inversion of configuration observed during rearrangement of **3a**.

momentum),[55] a purely dynamic phenomenon is operative in suitable systems (mostly bicyclic or polycyclic compounds) that carries the rearranging system via a *single* intermediate (e.g., a biradical) along a momentum-controlled reaction pathway to the products with predominantly inverted stereochemistry. As a consequence, the traditional models of kinetics do not apply, and the rearrangement shows a temperature-independent isomer ratio. In the rearrangement of **3a**, however, the *endo*-**10a**:*exo*-**12a** product ratio (Table VI) exhibits an appreciable change from 87:13 (−20 °C) to 77:23 (65 °C). Since the endo:exo ratio was shown to be time independent (Table VII), interconversion of the norbornenones should influence the ratios in Table VI only slightly. Consequently, no conservation of momentum effect seems to be operative.

A new hypothesis to understand the stereochemistry of the rearrangement of **3a** and **5a** is definitely needed. A tentative explanation is due to the possibility of stabilizing a radical center by an α-carbonyl group.[56] From AM1 calculations[43] it is proposed that in the ring-opened distonic cation radicals **22•⁺** and **23•⁺** the allyl moiety is much more easily oxidized than the α-carbonyl radical functionality.[57,58] As a consequence, cleavage of the C–C

bond results in the distonic cation radical **22•⁺** with an allyl cation and an α-carbonyl radical (Figure 4). The stabilization of the radical center by the carbonyl group now induces a twist motion and as a result of conservation of momentum effects favors the formation of the norbornenone cation radical with inversion of configuration at the migrating center. Since two cation radical intermediates are involved in this hypothesis, the endo:exo product ratio is no longer expected to be temperature independent. Corroboration of this mechanistic proposal, however, has still to await the study of comparable vinylcyclobutanes with the C=O group replaced by CH₂.

But how can the above hypothesis be accepted although retention of configuration is observed in the rearrangement of **9**? Apparently, when going from the bicyclic to the monocyclic vinylcyclobutanone, a change in the mechanism may take place, for which two explanations are conceivable. First, upon cleavage of the C–C bond in **9•⁺** to yield a distonic cation radical[59] a least motion rearrangement to **14•⁺** (eq 26a) is much faster than any

$$(26)$$

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(57) To elucidate the charge distribution in the open distonic cation radicals of **3a**–**6a**, we have calculated the adiabatic ionization potentials of the 1,2,3,4,5,5-hexamethylcyclopent-2-enyl radical (I_p = 6.86 eV) and of the 2-anisyl-3-oxobut-2-yl radical (I_p = 7.03 eV) by the AM1 method.[43] For the following discussion we assume similar solvation energies for both cations.

(58) This assumption is further corroborated by the observed analogous stereochemistry of the **3b**,**4b** rearrangement, proposing a similar intermediate as for the **3a**,**4a** rearrangement. Since in the tolyl system the α-carbonyl radical is certainly much more difficult to oxidize than the allyl radical, the open distonic cation radical most likely contains an allyl cation and α-carbonyl radical structure.

(59) The AM1 calculated adiabatic ionization potential of the 1,2,3,4-tetramethylpent-2-enyl radical (I_p = 7.11 eV), which serves as a model compound for the allyl radical part in the open distonic cation radical of **9**, is higher than that of the 2-anisyl-3-oxobut-2-yl radical (I_p = 7.03 eV). Thus, it is conceivable that the ring-opened **9•⁺** contains an α-carbonyl cation and an α-allyl radical moiety. Since stabilization of a planar conformation by an α-carbonyl group in the carbocation is much smaller than in a radical system, the twist motion has much less driving force: Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885.

Chart III

$7^{•+}$ $24^{•+}$

twist motion as a result of the much higher exergonicity for the reaction $9^{•+} \rightarrow 14^{•+}$ than for the reaction $3a^{•+} \rightarrow 10a^{•+}$.[60] Second, we cannot exclude that in the reaction $9^{•+} \rightarrow 14^{•+}$ a concerted rearrangement is operative (eq 26b), as claimed by Bauld[16] for structurally related vinylcyclobutanes (eq 20).

Vinylcyclobutanone Rearrangement: Scope. To assess the scope of the vinylcyclobutanone rearrangement, we studied the reactions of 7 (E_p = 1.61 V) in the presence of one-electron oxidants. Most importantly, rearrangement to **24** was not observed (eq 27), despite

(27)

7   24
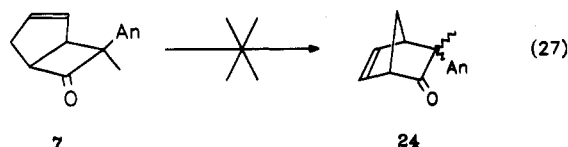
extensive variation in the solvents (acetonitrile, methylene chloride), the temperature (0 → 82 °C), and the one-electron oxidation systems (ET2 and PET with ET4, 1,4-dicyanobenzene, or 9,10-dicyanoanthracene). In all cases only polymeric products were formed.

The failure to rearrange 7 to 24 needs an explanation, since even **3b**, which exhibits a higher oxidation potential than 7, could successfully be rearranged. Two hypotheses can accommodate the experimental observations: (1) the wrong bond is cleaved in $7^{•+}$, or (2) the intermediate ring-opened cation radical does not close to norbornenone cation radical $24^{•+}$ (Chart III).

To test these proposals, vinylcyclobutanone 7 was reacted with 200 mol % ET2 in the presence of methanol. A GC/MS analysis detected five isomeric methoxylation products with m/z = 258. From their fragmentation patterns two basic structures could be derived (eq 28). The main products are cyclopentadienyl alkyl

200 mol% ET2

CH₃OH

7

(28)

+ isomers   + isomers
25   26
main   minor
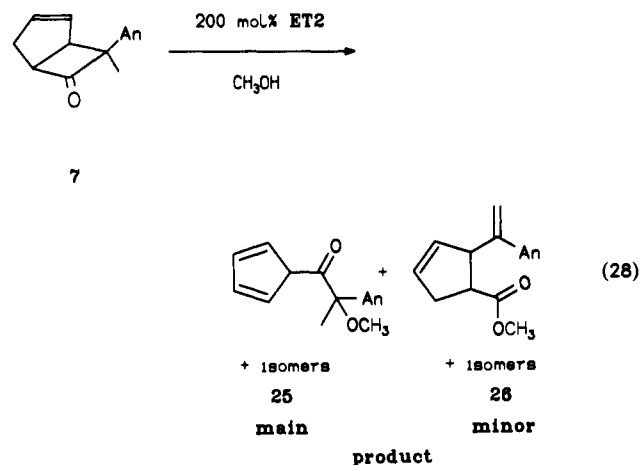
product

ketones **25** that originate from cleavage of bond 1, while only minor products, e.g., **26**, result from the rupture of bond 2. At present, we presume that methanol should not affect the selectivity for bond cleavage,[61] although there are indications in the literature of nucleophilic participation in carbon–carbon bond cleavage of cation radicals.[62] Thus, the correct bond for rearrangement is

broken in $7^{•+}$, but presumably the norbornenone cation radical $24^{•+}$ cannot form on energetic grounds. Since tertiary cations are much more stable than secondary ones, an alkyl group in position 4, as given in $10-12^{•+}$, to stabilize the intermediate $24^{•+}$ is a prerequisite for the rearrangement to occur.

Conclusion. Electron transfer constitutes a valuable tool to complement the thermal reaction pathways of ketenes and dienes, leading in general via a [2 + 2] cycloaddition to the vinylcyclobutanones. Two strategies, both based on cation radical catalysis, to react ketenes with dienes to form the DA products have been presented.

(1) The aminium salt initiated reaction of 1 and 2 to form the [4 + 2] products 10 and 12 proceeds at 0 °C within 5 min. No vinylcyclobutanones are formed. The reaction is assumed to proceed via intermediate cation radicals in a [3 + 2] cycloaddition.

(2) The cation radical vinylcyclobutanone rearrangement represents an intriguing, although indirect, way to ketene/diene DA products. Not only bicyclic, i.e., 3–6, but also monocyclic systems, i.e., 9, can be rearranged in good yields. A stereochemical analysis reveals that no frontier orbital control is operative. The observed predominant inversion of configuration with 3a and 5a is the result of a twist motion in the ring-opened cation radical $22a^{•+}$ as a consequence of radical stabilization by an α-carbonyl group. On the other hand, the stereochemical outcome of the rearrangement of 4a and 6a is a consequence of the high energy of $13a^{•+}$, thus directing the reaction exclusively to $11a^{•+}$. In the rearrangement 9 → 14 retention of configuration is observed. The failure to rearrange 7 to 24 could be rationalized by the necessity to stabilize the intermediate DA product cation radical.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra, in CDCl₃ unless specified otherwise, were obtained on Bruker WM 250 and AM 400 spectrometers, respectively. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. The numbering follows that given in Figure 1. Coupling constants $0.5 < J < 1.3$ Hz are listed as broadened signals. Mass spectra were obtained with a Finnigan MAT 44S instrument, and infrared spectra with a Perkin-Elmer 398 spectrometer using NaCl plates for liquid samples and CCl₄ solutions for solids. Melting points were determined with a Büchi capillary melting point apparatus (Dr. Tottoli) and are uncorrected. Elemental analyses were conducted by the University of Freiburg Microanalysis Facility. Gas chromatography analyses were performed on Carlo Erba Vega 6000 or Perkin-Elmer Sigma 2b chromatographs equipped with capillary columns. Chromatograms were recorded on a Hewlett-Packard 3393 A integrator. Preparative and analytical high-pressure liquid chromatography was performed on a Merck-Hitachi intelligent pump L-6200 that was hooked up to a Merck-Hitachi L-4200 UV–vis detector.

The AM1 calculations[43] were performed on a MicroVAX (Digital Equipment Corp.) computer using MOPAC 6.00 (Quantum Chemistry Program Exchange No. 455) and ChemX (Chemical Design Ltd.). Restricted Hartree–Fock (RHF) energies were calculated from single-point calculations of the optimized UHF geometries. The adiabatic ionization potentials were calculated from the total energy (RHF) difference of $M^{•+}$ and M.

The voltammetric experiments were performed in a homemade cell using a disk platinum working electrode (diameter: 1 mm), a helically wound platinum wire as auxiliary electrode, and a Ag/AgCl wire as reference electrode. A 10^{-3} M solution of the substrate was prepared in CH₃CN containing *tetra-n*-butylammonium hexafluorophosphate (0.1 M). The voltage sweep was controlled by a Princeton Applied Research 362 potentiostat. All potentials were referenced to ferrocene as internal standard with $E_{1/2}$ = 0.334 V using a scan rate of 0.1 V s⁻¹. Preliminary fast-scan cv studies were undertaken in the laboratory of Prof. J. P. Dinnocenzo (Rochester) using the setup developed by Prof. C. Amatore (Paris).[63]

Chemicals. To obtain purified acetonitrile,[64] the commercial product was successively refluxed from phosphorus pentoxide, potassium permanganate/lithium carbonate, potassium hydrogen sulfate, and calcium hydride and was finally distilled under purified argon. The dienes, except

(60) The free energies of the cation radical rearrangement in solution can be estimated via a thermochemical cycle by using calculated[7] heats of formation of the neutral compounds (assuming $\Delta G_R \approx \Delta H_R$) and the experimentally determined oxidation potentials: $\Delta G_R(9^{•+} \rightarrow 14^{•+})$ = −18 kcal mol⁻¹; $\Delta G_R(3a^{•+} \rightarrow 10a^{•+})$ = −10 kcal mol⁻¹.

(61) No nucleophilic participation of methanol was detected in the fragmentation of bicumene cation radicals: Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 8260.

(62) Ci, X.; Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 3893.

(63) Amatore, C.; Lefrou, C.; Pflüger, F. *J. Electroanal. Chem.* **1989**, *270*, 43.

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for **8**, were reagent grade commercial materials freshly distilled before use. (*E,E*)-3,4-Dimethylhexa-2,4-diene (**8**) was prepared from 2-butyne according to a literature procedure.[65] 2,6-Di-*tert*-butylpyridinium hexachloroantimonate was prepared from $HCl/SbCl_5$ and **15** in methylene chloride. Unless noted otherwise, all other reagents were used as received from commercial suppliers.

One-Electron Oxidants. The triarylamine ET1r was synthesized in 88% yield according to a method described by Gauthier,[66] whereas ET2r was obtained by bromination of triphenylamine.[67] The aminium hexachloroantimonates ET1a and ET2 were prepared by using a literature procedure given by Steckhan.[67] Alternatively, commercial ET2 was used after extensive rinsing with dry ether. ET1b was synthesized from triarylamine ET1r and nitrosonium hexafluoroantimonate in acetonitrile. At −70 °C the aminium salt could be stored for weeks. The synthesis of ET3 was accomplished according to the procedure of Kochi.[68] 1,4-Dicyanonaphthalene (ET4) was prepared from 1,2-bis(cyanomethyl)-benzene and 1,2-ethanediylidenebis(*N*-cyclohexylamine).[69]

(4-Methoxyphenyl)methylketene (1a). To a stirred solution of 2-(4-methoxyphenyl)propionic acid chloride (8.8 g, 44 mmol) in 40 mL of anhydrous diethyl ether was added at 0 °C 6.9 mL (49 mmol) of anhydrous triethylamine, dissolved in ether (40 mL), within 45 min. Stirring was continued for 15 h at 0 °C, and then the white precipitate was filtered from the yellow solution via Schlenk techniques. After the solvent had been removed in vacuo, the product was distilled (63 °C/0.1 Torr) to provide 4.7 g (66%, 29 mmol) of yellow, waxy solid **1a**: mp 30–35 °C; IR (CCl_4) 2100 cm^{-1}; ^{1}H NMR (250 MHz) δ 1.98 (s, 3 H, CH_3), 3.78 (s, 3 H, CH_3O), 6.89 (d, J = 9.0 Hz, 2 H, aryl-H), 6.95 (d, J = 9.0 Hz, 2 H, aryl-H); ^{13}C NMR (100 MHz) δ 9.0, 32.7, 55.4, 114.7, 124.8, 127.9, 156.7, 207.8.

(4-Methylphenyl)methylketene (1b). Following the procedure given above for the preparation of **1a**, 6.9 mL (49 mmol) of anhydrous triethylamine, dissolved in diethyl ether (40 mL), was added to a stirred solution of 2-(4-methylphenyl)propionic acid chloride (8.0 g, 44 mmol) in 40 mL of anhydrous diethyl ether at 0 °C. After distillation (50 °C, 0.01 Torr), 5.5 g (86%, 38 mmol) of **1b** was afforded. The isolated ketene is stable for only a few hours even at −20 °C; however, diluted solutions in CH_3CN can be stored at −20 °C for several days without decomposition: IR (CCl_4) 2080 cm^{-1}; ^{1}H NMR (250 MHz) δ 1.97 (s, 3 H, CH_3), 2.31 (s, 3 H, benzyl-CH_3), 6.91 (d, J = 9.0 Hz, 2 H, aryl-H), 7.13 (d, J = 9.0 Hz, 2 H, aryl-H).

Vinylcyclobutanones 3a–6a. To a solution of **2** (483 μL, 3.0 mmol) in benzene (3 mL) was added under argon 486 mg (3.0 mmol) of **1a**. The solution was heated to reflux for 2 days. After the solution cooled to room temperature, 2.0 mL of methanol was added and the solution stirred for 10 min. Thereafter the solvent was removed in vacuo, leaving 810 mg of crude product (91%). Homodimers of **1a** could be removed by recrystallization from petroleum ether at −25 °C. The remaining filtrate contained 640 mg (72%) of mostly the vinylcyclobutanone (54%). To isolate the vinylcyclobutanone, the crude mixture was first chromatographed over silica gel (Merck 0.041–0.063 mm, methylene chloride, R_f = 0.41–0.55) and then separated further by HPLC (reversed-phase, Merck LiChrosorb RP 18/7 μM; diameter, 25 mm; methanol:water = 9:1, 2.1 mL/min, t_R = 68–73 min) to yield 96 mg (11%) of a mixture of **3a** and **4a** (85:15): IR (CCl_4) 1765 cm^{-1}; ^{13}C NMR (100 MHz) δ 14.2, 14.4, 16.0 (C-8 to C-12), 20.6 (C-13), 48.6 (C-4), 55.3 (C-20), 58.9 (C-1), 67.4 (C-5), 70.1 (C-7), 113.1 (C-16, C-18), 128.0 (C-15, C-19), 132.6 (C-3), 135.8 (C-2), 137.2 (C-14), 158.3 (C-17), 223.9 (C-6); MS m/z 298 (2, M·$^+$), 162 (38, **1a**·$^+$), 136 (100, **2**·$^+$), 121 (78, 2-CH_3); HRMS calcd for $C_{20}H_{26}O_2$ (M·$^+$) 298.1926, found 298.1946. **3a**: ^{1}H NMR (250 MHz) δ 0.66 (br s, 3 H, 9-H), 0.87 (d, J = 7.2 Hz, 3 H, 11-H), 1.24 (s, 3 H, 8-H), 1.32 (s, 3 H, 12-H), 1.48 (br s, 3 H, 10-H), 1.60 (s, 3 H, 13-H), 2.72 (br q, J = 7.2 Hz, 1 H, 4-H), 3.75 (s, 3 H, 20-H), 6.74 (d, J = 9.2 Hz, 2 H, 16-H, 18-H), 6.95 (d, J = 9.2 Hz, 2 H, 15-H, 19-H). **4a**: ^{1}H NMR (250 MHz) δ 0.73 (br s, 3 H, 9-H), 1.18 (d, J = 7.2 Hz, 3 H, 11-H), 1.23 (s, 3 H, 8-H), 1.34 (s, 3 H, 12-H), 1.42 (br s, 3 H, 10-H), 1.52 (s, 3 H, 13-H), 2.34 (br q, J = 7.2 Hz, 1 H, 4-H), 3.75 (s, 3 H, 20-H), 6.74 (d, J = 9.2 Hz, 2H, 16-H, 18-H), 6.94 (d, J = 9.2 Hz, 2 H, 15-H, 19-H). From one cut taken after column chromatography **5a,6a** (t_R = 75–78 min) could also be isolated in 2% (14 mg) yield: IR (CCl_4) 1763 cm^{-1}; ^{13}C NMR (100 MHz) δ 12.0 (C-8, C-12), 15.6 (C-9, C-10), 18.1 (C-11), 22.3 (C-13), 29.8 (C-1), 48.2 (C-4), 55.3 (C-20), 67.8 (C-5), 72.4 (C-7), 113.7 (C-16, C-18), 128.2 (C-15, C-19),

134.4 (C-3), 137.9 (C-2, C-14), 158.1 (C-2), 223.6 (C-6); MS m/z 298 (1, M·$^+$), 162 (38, **1a**·$^+$), 136 (100, **2**·$^+$), 121 (93, 2-CH_3); HRMS calcd for $C_{20}H_{26}O_2$ (M·$^+$) 298.1926, found 298.1943. **5a**: ^{1}H NMR (250 MHz) δ 0.86 (d, J = 7.3 Hz, 3 H, 11-H), 0.92 (s, 3 H, 12-H), 1.01 (s, 3 H, 8-H), 1.28 (s, 3 H, 13-H), 1.62 (br s, 3 H, 9-H), 1.70 (br s, 3 H, 10-H), 2.75 (q, J = 7.3 Hz, 1 H, 4-H), 3.78 (s, 3 H, 20-H), 6.82 (d, J = 9.2 Hz, 2 H, 16-H, 18-H), 7.02 (d, J = 9.2 Hz, 2 H, 15-H, 19-H). **6a**: ^{1}H NMR (250 MHz) δ 0.79 (s, 3 H, 12-H), 1.08 (s, 3 H, 8-H), 1.11 (d, J = 7.3 Hz, 3 H, 11-H), 1.29 (s, 3 H, 13-H), 1.61 (br s, 3 H, 9-H), 1.70 (br s, 3 H, 10-H), 2.30 (q, J = 7.3 Hz, 1 H, 4-H), 3.78 (s, 3 H, 20-H), 6.82 (d, J = 9.2 Hz, 2 H, 16-H, 18-H), 7.04 (d, J = 9.2 Hz, 2 H, 15-H, 19-H).

Vinylcyclobutanones 3b–6b. A stirred solution of **1b** (438 mg, 3.0 mmol) and **2** (408 mg, 3.0 mmol) in 3.0 mL of anhydrous benzene was heated to reflux for 44 h under an argon atmosphere. Thereafter another 68 mg (0.5 mmol) of **2** was added, and heating was continued for 16 h. After the solution cooled to room temperature, 0.5 mL of methanol was added. After the solution was stirred for 1 h, all volatile compounds were removed in vacuo and the remaining oil was purified via chromatography (silica gel, Merck 0.041–0.063 mm, methylene chloride, R_f = 0.45–0.65), yielding 560 mg (63%) of almost pure **3b–6b**. To separate the endo and exo isomers, the mixture was chromatographed several times (reversed-phase HPLC, Merck LiChrosorb RP 18/7 μM; diameter, 25 mm; methanol:water:CH_3CN = 8:1:1, 4.5 mL/min, t_R = 51–68 min). The first fractions contained 70 mg of **3b,4b** in >99% purity (8%); the last fractions, pure (>99%) **5b,6b** (2%). The vinylcyclobutanones exhibited fast decomposition at room temperature and in daylight; therefore they were stored at −20 °C. **3b,4b**: IR (CCl_4) 1765 cm^{-1}; ^{13}C NMR (100 MHz) δ 14.3, 14.5, 16.0, 20.6, 21.1, 48.6, 58.9, 67.5, 70.4, 126.8, 128.4, 135.7, 136.1, 137.2, 137.4, 223.6; MS m/z 282 (6, M·$^+$), 146 (21, **1b**·$^+$), 136 (100, **2**·$^+$), 121 (71), 91 (23); MS (CI, NH_3) m/z 300 (43, M + NH_4^+), 283 (100, M + H$^+$); HRMS calcd for $C_{20}H_{26}O$ (M·$^+$) 282.1977, found 282.1970. **3b**: ^{1}H NMR (250 MHz) δ 0.65 (br s, 3 H, 9-H), 0.87 (d, J = 7.2 Hz, 3 H, 11-H), 1.24 (s, 3 H, 8-H), 1.32 (s, 3 H, 12-H), 1.47 (br s, 3 H, 10-H), 1.61 (s, 3 H, 13-H), 2.27 (s, 3 H, benzyl-CH_3), 2.72 (q, J = 7.2 Hz, 1 H, 4-H), 6.92 (d, J = 9.2 Hz, 2 H, 16-H, 18-H), 7.00 (d, J = 9.2 Hz, 2 H, 15-H, 19-H). **4b**: ^{1}H NMR (250 MHz) δ = 0.73 (br s, 3 H, 9-H), 1.18 (d, J = 7.2 Hz, 3 H, 11-H), 1.24 (s, 3 H, 8-H), 1.34 (s, 3 H, 12-H), 1.44 (br s, 3 H, 10-H), 1.53 (s, 3 H, 13-H), 2.27 (s, 3 H, benzyl-CH_3), 2.34 (q, J = 7.2 Hz, 1 H, 4-H), 6.91 (d, J = 9.2 Hz, 2 H, 16-H, 18-H), 7.00 (d, J = 9.2 Hz, 2 H, 15-H, 19-H). **5b,6b**: IR (CCl_4) 1765 cm^{-1}; MS m/z 282 (7, M·$^+$), 146 (45, **1b**·$^+$), 135 (56), 119 (100); MS (CI, NH_3) m/z 300 (31, M + NH_4^+), 283 (100, M + H$^+$); HRMS calcd for $C_{20}H_{26}O$ (M·$^+$) 282.1977, found 282.1980. **5b**: ^{1}H NMR (250 MHz) δ 0.85 (d, J = 7.3 Hz, 3 H, 11-H), 0.93 (s, 3 H, 12-H), 1.01 (s, 3 H, 8-H), 1.30 (s, 3 H, 13-H), 1.62 (br s, 3 H, 9-H), 1.70 (br s, 3 H, 10-H), 2.30 (s, 3 H, benzyl-CH_3), 2.75 (q, J = 7.3 Hz, 1 H, 4-H), 7.00 (d, J = 9.2 Hz, 2 H, 16-H, 18-H), 7.10 (d, J = 9.2 Hz, 2 H, 15-H, 19-H). **6b**: ^{1}H NMR (250 MHz) δ 0.79 (s, 3 H, 12-H), 1.07 (s, 3 H, 8-H), 1.11 (d, J = 7.3 Hz, 3 H, 11-H), 1.3C (s, 3 H, 13-H), 1.62 (br s, 3 H, 9-H), 1.70 (br s, 3 H, 10-H), 2.30 (s, 3 H, benzyl-CH_3), 2.30 (q, J = 7.3 Hz, 1 H, 4-H), 7.00 (d, J = 9.2 Hz, 2 H, 16-H, 18-H), 7.10 (d, J = 9.2 Hz, 2 H, 15-H, 19-H).

Vinylcyclobutanone 7. A solution of 4.0 g (25 mmol) of **1a** and 8.2 g (124 mmol) of freshly distilled cyclopentadiene in 25 mL of anhydrous benzene was stirred at room temperature for 48 h. After the volatile components were removed in vacuo, the remainder was recrystallized from *n*-hexane to yield 4.2 g (75%) of **7**: mp 55 °C; IR (CCl_4) 1772 cm^{-1}; ^{1}H NMR (250 MHz) δ 1.64 (s, 3 H, 8-H), 2.46 (m, 1 H, 4-H), 2.67 (m, 1 H, 4-H), 3.51 (m, 1 H, 1-H), 3.75 (s, 3 H, 15-H), 4.01 (m, 1 H, 5-H), 5.46 (m, 1 H, 2-H), 5.69 (m, 1 H, 3-H), 6.82 (d, J = 9.0 Hz, 2 H, 11-H, 13-H), 7.21 (d, J = 9.0 Hz, 2 H, 10-H, 14-H); ^{13}C NMR (100 MHz) δ 27.0, 34.3, 51.8, 55.2, 57.3, 80.0, 113.7, 127.3, 131.5, 132.8, 133.3, 158.1, 216.3; MS m/z 228 (6, M·$^+$), 213 (4, M − CH_3), 200 (7, M − CO), 185 (88, M − CO − CH_3), 162 (100, **1a**·$^+$), 134 (100, **1a** − CO); MS (CI, NH_3) m/z 229 (100, M + H$^+$), 162 (5, **1a**·$^+$). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.91; H, 7.08. Found: C, 78.98; H, 7.00.

Vinylcyclobutanone 9. A solution of 1.62 g (10 mmol) of **1a** in 2.26 mL (1.77 g, 16 mmol) of **8** was stirred at room temperature for 18 days. After the volatile components were removed in vacuo, the remaining oil was chromatographed (silica gel, Merck 0.05–0.2 mm, cyclohexane:ethyl acetate:triethylamine = 5:1:0.01, R_f = 0.50) to yield 1.42 g (52%) of pure, crystalline **9**: mp 67 °C; IR (CCl_4) 1769 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.77 (s, 3 H, 9-H), 1.10 (d, J = 7.2 Hz, 3 H, 10-H), 1.48 (s, 3 H, 8-H), 1.67 (br d, J = 6.5 Hz, 3 H, 7-H), 1.69 (br s, 3 H, 11-H), 3.75 (q, J = 7.2 Hz, 1 H, 4-H), 3.78 (s, 3 H, 18-H), 5.39 (br q, J = 6.5 Hz, 1 H, 6-H), 6.82 (d, J = 9.2 Hz, 2 H, 14-H, 16-H), 7.29 (d, J = 9.2 Hz, 2 H, 13-H, 17-H); ^{13}C NMR (100 MHz) δ 7.9, 13.4, 14.4, 20.4, 21.8, 47.9, 54.6, 55.1, 69.0, 113.3, 119.1, 128.7, 131.5, 138.7, 158.2, 215.2; MS m/z 272 (50, M·$^+$), 162 (100, **1a**·$^+$), 135 (100), 134 (100),

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119 (100), 95 (47, **8** – CH$_3$), 91 (100). Anal. Calcd for C$_{18}$H$_{24}$O$_2$: C, 79.36; H, 8.90. Found: C, 79.33; H, 8.87.

Norbornenones 10a and 12a. A solution of ET1a (350 mg, 0.56 mmol) in 5.0 mL of acetonitrile was added dropwise within 7 min to a solution of **2** (255 mg, 1.87 mmol) and **1a** (364 mg, 2.24 mmol) in 3.0 mL of acetonitrile held at 0 °C. The color of the solution changed during addition from yellow to, finally, a blue-brown hue. Stirring was continued for 45 min, and then a 2 N sodium methoxide solution in methanol was added until the blue color disappeared. Thereafter 150 mL of methylene chloride was added, and the organic layer was washed twice with 80 mL of brine. After the organic layer was dried (sodium sulfate), the solvent was removed in vacuo, thus providing an oil containing 56% **10a**, 15% **12a**, and 14% **18a**. After chromatography over silica gel (Merck 0.05–0.2 mm, methylene chloride, R_f = 0.25–0.36), which afforded 340 mg of crude **10a,12a** (61%), followed by preparative reversed-phase HPLC (Merck LiChrosorb RP 18/7 µm, i.d. = 25 mm, methanol:water = 9:1; flow, 2.1 mL min^{-1}; t_R = 76–85 min), 200 mg (36%) of pure **10a** and **12a** (purity > 99%) could be isolated. Separation of the two isomers was accomplished by repeating the reversed-phase HPLC several times (up to 20 times) and taking small fractions. Thus, isomerically pure material was obtained, i.e., 120 mg of **10a** (22%) and 25 mg of **12a** (5%). Data for **10a**: IR (CCl$_4$) 1733 cm^{-1} (C=O, vs); ^{1}H NMR (250 MHz) δ 0.76 (q, J = 1.3 Hz, 3 H, 11-H), 0.82 (d, J = 6.5 Hz, 3 H, 13-H), 1.08 (s, 3 H, 10-H), 1.14 (s, 3 H, 8-H), 1.40 (s, 3 H, 9-H), 1.54 (q, J = 1.3 Hz, 3 H, 12-H), 2.26 (q, J = 6.5 Hz, 1 H, 7-H), 3.75 (s, 3 H, 20-H), 6.72 (d, J = 9.1 Hz, 2 H, 16-H, 18-H), 6.83 (d, J = 9.1 Hz, 2 H, 15-H, 19-H); ^{13}C NMR (100 MHz) δ 7.6 (C-13), 9.3 (C-11), 10.0 (C-12), 10.5 (C-8), 12.1 (C-10), 20.5 (C-9), 55.0 (C-3), 55.3 (C-20), 56.7 (C-7), 57.8 (C-1), 64.8 (C-4), 112.8 (C-16, C-18), 126.9 (C-14), 128.5 (C-15, C-19), 136.2 (C-5), 144.4 (C-6), 157.8 (C-17), 217.1 (C-2); MS m/z 298 (1, M$^{•+}$), 270 (2, M – CO), 162 (13, **1a**$^{•+}$), 136 (100, **2**$^{•+}$), 121 (48, **2** – CH$_3$); MS (CI, NH$_3$) m/z 316 (24, M + NH$_4$$^+$), 299 (100, M + H$^+$), 162 (4, **1a**$^{•+}$), 136 (24, **2**$^{•+}$). Anal. Calcd for C$_{20}H_{26}O_2$: C, 80.48; H, 8.80. Found: C, 80.69; H, 8.85. Data for **12a**: IR (CCl$_4$) 1733 cm^{-1} (C=O, vs); ^{1}H NMR (250 MHz) δ 0.74 (d, J = 6.5 Hz, 3 H, 13-H), 0.98 (s, 3 H, 10-H), 1.14 (s, 3 H, 8-H), 1.35 (s, 3 H, 9-H), 1.52 (q, J = 1.3 Hz, 3 H, 12-H), 1.72 (q, J = 1.3 Hz, 3 H, 11-H), 2.25 (q, J = 6.5 Hz, 1 H, 7-H), 3.78 (s, 3 H, 20-H), 6.79 (d, J = 9.1 Hz, 2 H, 16-H, 18-H), 6.96 (d, J = 9.1 Hz, 2 H, 15-H, 19-H); ^{13}C NMR (100 MHz) δ 7.1 (C-13), 8.9 (C-11), 10.2 (C-12), 11.6 (C-8), 13.3 (C-10), 22.8 (C-9), 55.3 (C-20), 55.8 (C-3), 56.9 (C-7), 57.3 (C-1), 64.1 (C-4), 113.0 (C-16, C-18), 129.4 (C-15, C-19), 129.9 (C-14), 134.9 (C-5), 143.7 (C-6), 157.8 (C-17), 220.3 (C-2); MS m/z 162 (11, **1a**$^{•+}$), 136 (100, **2**$^{•+}$), 121 (50, **2** – CH$_3$); MS (CI, NH$_3$) m/z 316 (16, M + NH$_4$$^+$), 299 (100, M + H$^+$), 281 (12), 162 (3, **1a**$^{•+}$), 136 (18, **2**$^{•+}$). Anal. Calcd for C$_{20}$H$_{26}$O$_2$: C, 80.48; H, 8.80. Found: C, 80.22; H, 8.67.

Norbornenone 11a. To a solution of 16.0 mg (0.054 mmol) of **3a,4a** (85:15) and **15** (5.7 mg, 0.030 mmol) in 0.15 mL of acetonitrile was added a suspension of ET2 (22.0 mg, 0.027 mmol) in 0.15 mL of acetonitrile. After the mixture was stirred for 5 min at 0 °C, the reaction was quenched by addition of a methoxide solution in methanol, whereupon the color changed from blue to yellow. ^{1}H NMR showed three products; two of them had been identified earlier as **10a** and **12a**. Despite several attempts to isolate the unknown product (13%)[27] by chromatography, only material admixed with **10a** and **12a** could be obtained. Data for **11a**: IR (CCl$_4$) 1733 cm^{-1} (C=O, vs); ^{1}H NMR (250 MHz) δ 0.70 (q, J = 1.3 Hz, 3 H, CH$_3$—C=C), 0.93 (d, J = 6.5 Hz, 3 H, C*H*$_3$CH), 1.15 (s, 3 H, CH$_3$), 1.25 (s, 3 H, CH$_3$), 1.40 (s, 3 H, CH$_3$), 1.52 (q, J = 1.3 Hz, 3 H, CH$_3$—C=C), 1.99 (q, J = 6.5 Hz, 3 H, C*H*CH$_3$), 3.74 (s, 3 H, CH$_3$O), 6.70–6.83 (2 d, J = 9.1 Hz, 4 H, aryl-H).

Norbornenones 10b and 12b. A suspension of ET2 (548 mg, 0.7 mmol) in 5 mL of acetonitrile was added within 5 min to a solution of **1b** (350 mg, 2.4 mmol) and **2** (272 mg, 2.0 mmol) in acetonitrile (3 mL) at 0 °C. The reddish brown mixture was stirred for 15 min, and then a brine solution (20 mL) was added. The organic products were extracted with methylene chloride, and the combined organic layers were dried with sodium sulfate. Rotary evaporation of the solvent afforded 530 mg of a crude product mixture, containing 25% **10b,12b**. Use of preparative HPLC (Merck LiChrosorb RP 18/7 µm, i.d. = 25 mm, methanol:water = 9:1; flow, 3.0 mL/min) allowed pure **10b,12b** to be isolated in 4% yield. Despite several attempts, we were unable to separate the isomers. At room temperature the mixture of **10b** and **12b** decomposed within a few days. Data for **10b,12b**: IR (CCl$_4$) 1734 cm^{-1} (vs, C=O); ^{13}C NMR (100 MHz) δ 7.5, 9.3, 10.0, 10.5, 12.2, 20.5, 22.7, 56.7, 56.8, 57.8, 64.9, 127.4, 128.4, 135.8, 137.0, 137.3, 144.2, 217.8 (only one set of signals was observed in a mixture of **10b:12b** = 70:30); MS m/z 282 (2, M$^{•+}$), 136 (100, **2**$^{•+}$), 121 (83, **2** – CH$_3$), 119 (20), 105 (21), 91 (22); MS (CI, NH$_3$) m/z 300 (100, M + NH$_4$$^+$), 283 (14, M + H$^+$), 136 (8, **2**$^{•+}$); HRMS calcd for C$_{20}H_{26}$O (M$^{•+}$) 282.1977, found 282.1981. Data for **10b**: ^{1}H NMR (250 MHz) δ 0.70 (q, J = 1.3 Hz,

3 H, 11-H), 0.82 (d, J = 6.5 Hz, 3 H, 13-H), 1.08 (s, 3 H, 10-H), 1.13 (s, 3 H, 8-H), 1.40 (s, 3 H, 9-H), 1.51 (q, J = 1.3 Hz, 3 H, 12-H), 2.25 (s, 3 H, benzyl-CH$_3$), 2.27 (q, J = 6.5 Hz, 1 H, 7-H), 6.78 (d, J = 9.1 Hz, 2 H, 16-H, 18-H), 6.98 (d, J = 9.1 Hz, 2 H, 15-H, 19-H). Data for **12b**: ^{1}H NMR (250 MHz) δ 0.70 (d, J = 6.5 Hz, 3 H, 13-H), 0.97 (s, 3 H, 10-H), 1.13 (s, 3 H, 8-H), 1.34 (s, 3 H, 9-H), 1.51 (q, J = 1.3 Hz, 3 H, 12-H), 2.25 (q, J = 6.5 Hz, 1 H, 7-H), 2.25 (s, 3 H, 20-H), 6.72 (d, J = 9.1 Hz, 2 H, 16-H, 18-H), 7.04 (d, J = 9.1 Hz, 2 H, 15-H, 19-H).

Cyclohexenone 14. A suspension of ET2 (98 mg, 0.12 mmol) in acetonitrile was added dropwise over a period of 10 min to a solution of **9** (65 mg, 0.24 mmol) and **15** (25 mg, 0.13 mmol) in 1.0 mL of acetonitrile at room temperature. Stirring was continued for another 10 min, and then the brown solution was concentrated in vacuo. The remainder was chromatographed on silica gel (Merck 0.05–0.2 mm, cyclohexane:ethyl acetate:triethylamine = 5:1:0.01, R_f = 0.45), affording 43 mg (65%) of pure **14**: IR (CCl$_4$) 1710 cm^{-1} (vs, C=O); ^{1}H NMR (250 MHz) δ 0.75 (d, J = 7.2 Hz, 3 H, 8-H), 1.28 (d, J = 7.2 Hz, 3 H, 11-H), 1.51 (s, 3 H, 7-H), 1.70 (br s, 3 H, 10-H), 1.75 (br s, 3 H, 9-H), 2.26 (br q, J = 7.2 Hz, 1 H, 3-H), 2.86 (br q, J = 7.2 Hz, 1 H, 6-H), 3.78 (s, 3 H, 18-H), 6.82 (d, J = 9.2 Hz, 2 H, 14-H, 16-H), 7.21 (d, J = 9.2 Hz, 2 H, 13-H, 17-H); ^{13}C NMR (100 MHz) δ 15.4, 16.9, 18.2, 18.6, 25.7, 46.6, 49.4, 55.2, 55.3, 113.1, 126.7, 129.4, 131.4, 134.1, 157.9, 214.8; MS m/z 272 (4, M$^{•+}$), 162 (54, **1a**$^{•+}$), 135 (100), 84 (47), 43 (82); MS (CI, NH$_3$) m/z 273 (69, M + H$^+$), 151 (100). Anal. Calcd for C$_{18}$H$_{24}$O$_2$: C, 79.36; H, 8.90. Found: C, 79.48; H, 8.82.

Cyclohexenone 21. Trifluoromethanesulfonic acid (43.2 mg, 0.288 mmol) was added to a solution of **9** (52.1 mg, 0.191 mmol) in 2.0 mL of acetonitrile at 0 °C under argon. The yellow solution was stirred for 5 min, and then 20 mL of brine was added. After extraction with methylene chloride, the combined organic layers were dried (sodium sulfate) and concentrated by rotary evaporation. The remaining oil was chromatographed over silica gel (Merck 0.05–0.2 mm, cyclohexane:ethyl acetate:triethylamine = 2:1:0.01, R_f = 0.60) to afford 25.0 mg of pure **21** (48%): IR (CCl$_4$) 1663 cm^{-1} (vs, C=O); ^{1}H NMR (250 MHz) δ 0.74 (d, J = 7.0 Hz, 3 H) and 0.96 (d, J = 7.0 Hz, 3 H) (9-H and 10-H, respectively), 1.51 (s, 3 H, 11-H), 1.90 (q, J = 1.4 Hz, 3 H) and 1.92 (q, J = 1.4 Hz, 3 H) (7-H, 8-H), 2.18 (m, 1 H) and 2.46 (m, 1 H) (4-H, 5-H), 3.75 (s, 3 H, 18-H), 6.75 (d, J = 9.0 Hz, 2 H, 14-H, 16-H), 7.03 (d, J = 9.0 Hz, 2 H, 13-H, 17-H); ^{13}C NMR (100 MHz) δ 11.9, 13.5, 17.3, 19.9, 25.1, 39.8, 43.7, 51.9, 55.2, 113.2, 128.6, 129.5, 130.5, 136.5, 157.9, 202.6; MS m/z 272 (7, M$^{•+}$), 162 (44, **1a**$^{•+}$), 110 (100, **8**$^{•+}$); HRMS calcd for C$_{18}$H$_{24}$O (M$^{•+}$) 272.1770, found 272.1772. Anal. Calcd for C$_{18}$H$_{24}$O: C, 79.36; H, 8.90. Found: C, 79.19; H, 8.81.

^{1}H NMR NOE Experiments. All difference NOE experiments have been done with the 400-MHz instrument using argon-saturated solutions of the samples in CDCl$_3$. The individual results are depicted in the following way: ⟶irradiated H (⊕ = positive NOE effect; ⊖ = no NOE effect). **3a**: ⟶4-H (⊕ 10-H, 11-H, aryl-H), ⟶8-H (⊕ 9-H, 12-H, 13-H, aryl-H, ⊖ 4-H, 10-H, 11-H), ⟶9-H (⊕ 10-H, aryl-H), ⟶10-H (⊕ 4-H, 9-H, 11-H, aryl-H), ⟶11-H (⊕ 4-H, 10-H, 12-H, negative NOE for aryl-H), ⟶12-H (⊕ 4-H, 8-H, 11-H, 13-H, ⊖ aryl-H), ⟶13-H (⊕ 8-H, 12-H, aryl-H). **9**: ⟶4-H (⊕ 6-H, 10-H, negative NOE for 7-H), ⟶6-H (⊕ 4-H, 7-H), ⟶7-H (⊕ 6-H, negative NOE for 4-H), ⟶8-H (⊕ 4-H, 11-H, aryl-H), ⟶9-H (⊕ 10-H, 11-H, aryl-H), ⟶10-H (⊕ 4-H, 9-H, aryl-H), ⟶11-H (⊕ aryl-H), ⟶aryl-H (⊕ 8-H, 11-H, aryl-H). **10a**: ⟶7-H (⊕ 8-H, 9-H, 10-H, 13-H; ⊖ 11-H, 12-H, aryl-H), ⟶8-H (⊕ 7-H, 12-H, 13-H), ⟶9-H (⊕ 7-H, aryl-H), ⟶10-H (⊕ 7-H, 11-H, 13-H, aryl-H), ⟶11-H (⊕ 10-H, 12-H, aryl-H), ⟶12-H (⊕ 11-H, aryl-H), ⟶aryl-H (⊕ 9-H, 10-H). **12a**: ⟶8-H (⊕ 7-H, 12-H, 13-H), ⟶9-H (⊕ 11-H, aryl-H, negative NOE for 7-H), ⟶10-H (⊕ 7-H, 11-H, 13-H, aryl-H, negative NOE for 8-H), ⟶11-H (⊕ 12-H), ⟶12-H (⊕ 11-H), ⟶13-H (⊕ 7-H, 8-H, 10-H, negative NOE for aryl-H), ⟶aryl-H (⊕ 7-H, 8-H, 9-H, 10-H). **14**: ⟶3-H (⊕ 6-H, 8-H, 9-H), ⟶6-H (⊕ 3-H, 10-H, 11-H), ⟶7-H (⊕ 3-H, 6-H, aryl-H), ⟶8-H (⊕ 3-H, 9-H, aryl-H), ⟶9-H (⊕ 3-H), ⟶10-H (⊕ 6-H, 11-H), ⟶11-H (⊕ 6-H, 10-H), ⟶aryl-H (⊕ 3-H, 7-H).

Mechanistic Studies. (a) Thermal Cycloaddition of 1a and 2. A solution of **1a** (243 mg, 1.50 mmol) and **2** (203 mg, 1.50 mmol) in 1.50 mL of argon-saturated benzene was heated to reflux. Samples were taken every 24 h for 9 days and analyzed by ^{1}H NMR vs *m*-nitroacetophenone as internal standard. The best yield of **3a–6a** (54%) was obtained after 2–3 days.

(b) Thermal Cycloaddition of 1b and 2. Compounds **1b** (100 mg, 0.68 mmol) and **2** (125 mg, 0.92 mmol) were dissolved in benzene and heated to reflux for 66 h. Samples taken every 24 h indicated that 37% of **3b–6b** had formed after 44 h.

(c) Cycloaddition in the Presence of One-Electron Oxidants. All reactions were performed in a septum-closed Schlenk tube under argon.

Via syringe techniques a solution of the ketene and diene (and, if necessary, of **15**) in acetonitrile was placed in the tube. Unless noted differently, a solution or a suspension of the one-electron oxidant was added dropwise at 0 °C within a maximum of 2 min. Thereupon, the reaction mixture was stirred for a total of 5 min. Finally, the reaction was quenched by the dropwise addition of a 2 N NaOCH₃/CH₃OH solution. Within 60 s, 30 mL of brine was added, and the products were extracted three to five times using a total of 100 mL of methylene chloride. The combined organic layers were dried (sodium sulfate) and the solvent removed in vacuo. To the crude product mixture was added a known amount of *m*-nitroacetophenone, if necessary, and the mixture was analyzed by ¹H NMR and GC. When ET3 was used as the one-electron oxidant, then the reaction was quenched by addition of 0.50 mL methanol (stirred for 15 min). After removal of all volatile components, the remainder was extracted with benzene or ether to separate off the iron salts. After removal of the solvent, the crude mixture was analyzed as noted above. The results of the cycloadditions are provided in Tables I and II. Control experiments using Lewis acids were run following the above procedure, but the reactions were quenched by addition of water.

(d) Cycloaddition and Vinylcyclobutanone Rearrangement under PET Initiation. A solution of ketene **1** (0.2–0.5 mmol), diene **2**, and the acceptor/biphenyl system was prepared in 0.5 mL of argon-flushed acetonitrile (or *d*₃-acetonitrile). The mixture was irradiated in a Pyrex tube at λ > 350 nm for the indicated time periods. To quench the ketene several drops of methanol were added, and the volatile components were removed in vacuo. The mixture was analyzed by ¹H NMR (Table III). Similarly, the PET-induced vinylcyclobutanone rearrangement was performed, the results of which are presented in Table V.

(e) Vinylcyclobutanone Rearrangement in the Presence of One-Electron Oxidants. According to the conditions noted above under paragraph c, the solution of vinylcyclobutanone and **15** in acetonitrile was placed in a Schlenk tube, and a solution of the one-electron oxidant was added dropwise. After workup the mixture was analyzed by ¹H NMR (Table V). Control experiments to evaluate the configurational stability of **10a**

and **12a** as well as of **3a–6a** were conducted under the above conditions (Table VII).

(f) Stoichiometric Oxidation of 7 in the Presence of Methanol. To a solution of ET2 (82.0 mg, 0.100 mmol) in acetonitrile (0.50 mL) was added a solution of **7** (11.4 mg, 0.050 mmol) dissolved in 0.3 mL of methanol and 0.1 mL of acetonitrile. After 15 min at room temperature the color of the mixture changed from blue to a turbid, gray bluish hue. The reaction mixture was stirred for another 10 min, and then it was quenched. After standard workup the mixture was analyzed by ¹H NMR, indicating recovery of 55% of **7**. The products were analyzed by GC/MS using cold-on-column techniques. Six products, a–f, could be identified by their MS data. Product a (55%) was identified as **7**. Product b (8%): MS *m/z* 258 (4, M⁺⁺), 244 (5, M – CH₂), 230 (5, M – CO), 215 (20, M – CO – CH₃), 199 (26, M – CO – OCH₃), 151 (44, M – An), 135 (49), 66 (33, Cp), 43 (54), 40 (100); MS (CI, NH₃) *m/z* 259 (3, M + H⁺), 245 (24, M + H – CH₂), 227 (100, M – CH₃O). Product c (10%): MS *m/z* 165 (100, C(An)(CH₃)(OCH₃)⁺), 135 (11), 43 (28); MS (CI, NH₃) *m/z* 259 (37, M + H⁺), 227 (12), 199 (8), 165 (100), 151 (25). Product d (8%): MS *m/z* 165 (100, C(An)(CH₃)-(OCH₃)⁺), 135 (12), 43 (34); MS (CI, NH₃) *m/z* 259 (54, M + H⁺), 227 (12), 199 (9), 165 (100), 151 (14). Product e (11%): MS *m/z* 165 (100, C(An)(CH₃)(OCH₃)⁺), 135 (12), 43 (43); MS (CI, NH₃) *m/z* 259 (100, M + H⁺), 227 (3), 199 (8), 165 (6), 151 (3). Product f (5%): MS *m/z* 165 (100, C(An)(CH₃)(OCH₃)⁺), 135 (12), 43 (45); MS (CI, NH₃) *m/z* 259 (100, M + H⁺), 227 (15), 199 (10), 165 (87), 151 (12).

Cooperative Effect of Acid Sites in the Photocyclization of Azobenzene within the Zeolite Microenvironment

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Abstract: Photolysis of azobenzene in the presence of a series of acidic zeolites with different crystal size (0.8 and 0.3 μm), crystalline structure (Y, β, ZSM-5), and framework Si-to-Al ratio (Al/cage ranging from 4.6 to 0.25) gives rise to benzo[c]cinnoline and benzidine. The latter remains protonated within the zeolite cavities, as has been established by FT-IR spectroscopy of the hosts. The lack of influence of the crystallite size on the activity of the zeolite reveals that the reaction is mainly taking place on the internal surface of these microporous solids. Finally, the relationship between the activity of the zeolite and the number of Brönsted sites per α-cage indicates that only two H⁺ per supercavity can participate in the photocyclization of azobenzene. This result agrees with the relative size of the zeolite cavities and the reactant molecules.

Introduction

The photochemistry of organic compounds within the voids and cavities of zeolites has recently emerged as one of the most promising tools to gain control of the different pathways undergone by the excited states.[1-3]

The main advantage of zeolites as "microscopic reactors" is that these photostable microporous solids can be synthesized in a large variety of crystalline structures and chemical compositions, thus providing a series of well-characterized isotropic materials with strictly regular properties.

Up to now, the majority of the photochemical studies within zeolites have made use of these materials just as a vessel of molecular dimensions to restrict the motions of the reaction intermediates (radicals). However, the possibilities of zeolites can be enlarged by making them directly intervene during the course of the photochemical reaction due to the presence in the internal voids of charge-compensating cations which can act as active sites.

In the present paper we describe the influence of the chemical environment of the zeolite host on the photocyclization of azobenzene (AB) to benzo[c]cinnoline (BC) adsorbed on a series of acid zeolites with different particle size, crystalline structure, and framework Si-to-Al ratio. To the best of our knowledge, this constitutes the first example where a cooperative contribution of

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