

Olefin Radical Cation Cycloadditions¹⁾

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Radical-cation cyclodimerizations of electron-rich cyclic 1,3-dienes and radical-cation Diels-Alder reactions of these dienes with several electron-rich olefins have been investigated. In some cases the efficiency of the electron transfer could be increased if the electron acceptors were combined with LiClO₄ (special salt effect). The dimerization of 1,3-cyclohexadiene (**7a**), as well as 1-acetoxy- and 1-methoxy-1,3-cyclohexadiene (**7b**, **7c**) with several electron acceptors yielded *endo*-selectively the Diels-Alder dimers. The formation of the Diels-Alder products via radical-ion intermediates could be demonstrated by quenching experiments. In addition, cyclobutane dimers were also formed, mostly through triplet-reaction channels. Only in the case of 1-acetoxy-1,3-cyclohexadiene (**7b**) photochemically induced electron transfer is involved as well, as shown by quenching experiments. Some of these Diels-Alder dimerizations are indicated by a characteristic concentration dependence, i.e. the *endo* [2+4] dimers were preferably formed at low diene concentrations, whereas high diene concentrations favored the *exo* [2+4] adducts. In the reaction sensitized by 1,4-dicyanophthalene (**2**) these concentration effects could be emphasized by differently strong quenching of the different products. Concentration and quenching effects indicate the involvement of different radical-ion intermediates. Crossed Diels-Alder reactions usually ran *endo*-selectively. Here, quenching of product formation with 1,2,4-trimethoxybenzene (TMB) indicated the involvement of radical intermediates as well.

Cycloadditionen von olefinischen Radikalkationen

Radikalkation-katalysierte Cyclodimerisierungen elektronenreicher, cyclischer 1,3-Diene sowie radikalkation-katalysierte Diels-Alder-Reaktionen dieser Diene mit verschiedenen elektronenreichen Olefinen wurden untersucht. Die Effizienz des Elektronentransfers konnte in einigen Fällen durch Kombination der Elektronenakzeptoren mit LiClO₄ erhöht werden (spezieller Salzeffekt). Die Dimerisierungen von 1,3-Cyclohexadien (**7a**) sowie 1-Acetoxy- und 1-Methoxy-1,3-cyclohexadien (**7b**, **7c**) mit verschiedenen Elektronenakzeptoren lieferten *endo*-selektiv die jeweiligen Diels-Alder-Dimeren. Durch Löschemperimente konnte gezeigt werden, daß die Diels-Alder-Produkte über radikalionische Zwischenstufen gebildet wurden. In einigen Fällen wurden ebenfalls Cyclobutan-Dimere gebildet – meist über Triplett-Reaktionskanäle. Nur mit 1-Acetoxy-1,3-cyclohexadien (**7b**) verläuft die Cyclobutan-Dimerisierung auch über photochemisch induzierten Elektronentransfer wie entsprechende Löschemperimente zeigten. Einige dieser Diels-Alder-Reaktionen weisen eine charakteristische Konzentrationsabhängigkeit auf, d.h. bei niedrigen Dien-Konzentrationen wurden überwiegend *endo*-[2+4]-Dimere gebildet, während höhere Dien-Konzentrationen die Bildung der *exo*-[2+4]-Addukte begünstigten. Diese Konzentrationseffekte konnten in den durch 1,4-Dicyanonaphthalin (**2**) sensibilisierten Reaktionen durch unterschiedlich starke Löschung der verschiedenen Produkte unterstrichen werden. Konzentrations- und Löschemeffekte deuten darauf hin, daß verschiedenartige radikalionische Zwischenstufen beteiligt sind. Gemischte Diels-Alder-Reaktionen verliefen in der Regel ebenfalls *endo*-selektiv. Die Löschung der Produktbildung mit 1,2,4-Trimethoxybenzol (TMB) deutete auch hier auf die Beteiligung radikalionischer Zwischenstufen hin.

1. Introduction

One of the most important cycloadditions in organic chemistry is the Diels-Alder reaction²⁾. Its scope of application, however, is limited by one of the fundamental rules of thermal [4 π +2 π] cycloadditions: namely, a sufficiently high reaction rate is only achieved if the frontier orbitals of the starting materials (HOMO and LUMO) are energetically close³⁻⁴⁾. Such ideal conditions are not always fulfilled, and there has therefore been no lack of attempts to find improvements for Diels-Alder reactions that yield poor results. Examples include reactions under high pressure conditions⁵⁻⁸⁾, catalysis by Lewis acids⁹⁻¹¹⁾, reactions via cations¹²⁾, and the exploitation of the hydrophobic effect for reactions in aqueous media^{13,14)}. The importance of charge-transfer interactions between diene and dienophile in the transition state of Diels-Alder cycloadditions is described by Sustmann^{15a)} and Kochi^{15b)}. A further approach makes use of the following principle: Oxidation of one of the reacting species to a radical cation results in an increase of the frontier-orbital interaction which should in turn lead to an acceleration of the Diels-Alder reaction¹⁶⁾. Such an oxidation can,

for example, be achieved by photochemically induced electron transfer within a donor-acceptor pair^{17,18)}.

The importance of electron transfer in photochemistry has been known ever since the fundamental work of Weller^{19a)} and, for instance, the studies of Marcus^{19b)} and Hush^{19c)}. Among the first examples of photochemically induced reactions of olefin radical cations was the dimerization of *N*-vinylcarbazole, first discovered by Ellinger²⁰⁾ and later thoroughly investigated by Ledwith^{21,22)}. Other dimerizations have been described by Farid²³⁾, Arnold²⁴⁾, Pac^{25,26)}, and others^{27,28)}. As Freeman²⁹⁾ and Hammond³⁰⁾ have shown, the radiation-induced dimerization of 1,3-cyclohexadiene, reported by Schenck³¹⁾ can also be explained as a cycloaddition involving radical cations. A similar effect was observed by Mizuno³²⁾ in the Diels-Alder reaction of furan with indene in presence of naphthalene carbonitriles as photochemical electron acceptors. According to Mizuno³²⁾, this reaction proceeds by an electron-transfer mechanism. If that process involves electron-transfer back from the acceptor-radical anion to the product-radical cation, the mechanism is called electron-transfer sensitization³³⁾ (see Figure 1a). In polar

solvents, the compounds of a contact-ion pair can be "separated" by solvation to form either a solvent-separated radical-ion pair or free radical ions^{17,34}. The process may be enhanced by the salt effect: In some cases lifetime and yield of radical ions can be greatly increased by ion-exchange reactions^{17,34} (further reports on the special salt effect see ref.³⁴⁻⁴²). This hindrance of the back-electron transfer often allows the deliberate production of radical ions and thereby allows the study of their reactions without the involvement of the radical-ion partner, i.e., without chemical reaction¹⁷. The thermodynamics of electron transfer within a donor-acceptor system can be estimated by the Weller equation (eq. 1):

$$\Delta G(A_5^{\cdot-} \cdot D_5^{\cdot+}) = F[E_{1/2}^{ox}(D) - E_{1/2}^{red}(A)] - \Delta E_{excit} + \Delta E_{coul} \quad (1)$$

$E_{1/2}^{ox}(D)$ and $E_{1/2}^{red}(A)$ are the oxidation potential of the donor and the reduction potential of the acceptor, respectively, measured in acetonitrile; ΔE_{excit} is the excitation energy of the electronically excited species, and ΔE_{coul} the Coulomb interaction energy of the two radical ions⁴³⁻⁴⁵. Later Bauld⁴⁶ applied the principle of photochemically induced electron-transfer reactions to thermal electron acceptors and coined the term "cation-radical-catalyzed Diels-Alder reaction"; this reaction is based on a chain mechanism (see Figure 1 b). For most recent results on the kinetics of the cyclohexadiene dimerization cf. "Note added in proof".

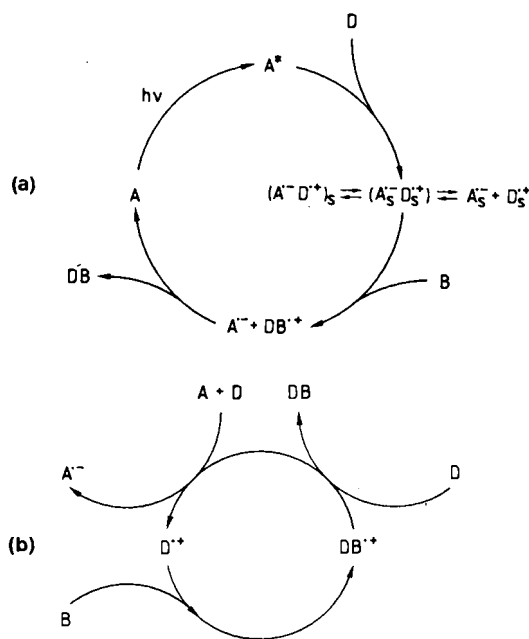


Figure 1. Electron-transfer sensitization (a) and chain mechanism (b) in radical-cation reactions (A: acceptor; D, B: donors)

According to the theoretical considerations of Bauld, the radical-cation-catalyzed Diels-Alder reaction should obey the "principle of role selectivity", which states that the cycloaddition occurs preferably by means of the radical cation of the dienophile⁴⁶. Since then many groups have concerned themselves with this problem. So Gross⁴⁸, Roth⁴⁹, Schuster⁵⁰, Steckhan⁵¹, Mattay⁵²⁻⁵⁶, and finally also Bauld^{16,57} have found evidence for a multistep mechanism. That means that the radical-cation-catalyzed Diels-Alder reaction can proceed not only via the radical cation of the dienophile but also via the radical cation of the diene. A further, more detailed discussion is described in a recent review from this laboratory¹⁷. In this work⁵⁶, several electron-transfer-sensitized cyclodimeriza-

tions and crossed Diels-Alder reactions are described, especially with regard to the influence of different radical-ion intermediates.

2. Results and Discussion

2.1. Cyclodimerizations

2.1.1. 1,3-Cyclohexadiene (7a)

The radical-cation Diels-Alder dimerization of **7a** was first described by Schenck³¹. Later, Freeman²⁹ and Hammond³⁰ independently identified this dimerization as a radical-cation chain reaction. In 1981, Bauld⁴⁶ described the radical-cation chain dimerization of **7a** in presence of tri(*p*-bromophenyl)ammoniumyl hexachloroantimonate (**1**) as electron acceptor. Later, Jones⁵⁹ observed that irradiation of dicyanoanthracene in a methylene chloride solution containing **7a** gives the [4+2] dimers of **7a**. Dimerization of **7a** via a ternary complex (triplex) in a nonpolar solvent has been reported by Schuster⁶⁰. Further studies on the radical-cation dimerization of **7a** have been described by Steckhan⁶¹ who used 2,4,6-triphenylpyrylium tetrafluoroborate (**6**) as electron acceptor and by Gassman¹² who studied the influence of acid catalysis on Diels-Alder reactions. A recent study by Laszlo and Lucchetti⁶² of the dimerization of **7a** initiated by ferric ion trapped in a clay matrix also implicates the participation of a radical-cation Diels-Alder chain mechanism. Our group has investigated the dimeriza-

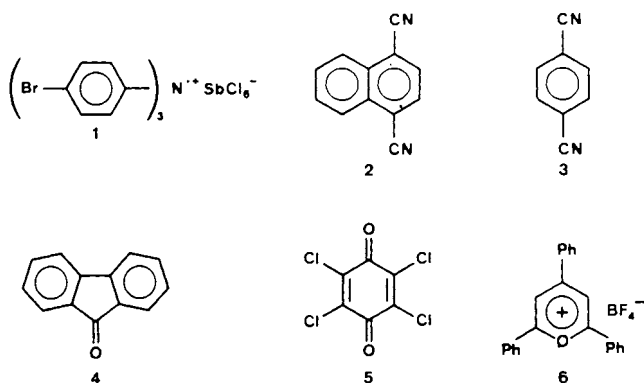


Figure 2. Electron-acceptor molecules: tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate (**1**), 1,4-dicyanonaphthalene (**2**), 1,4-dicyanobenzene (**3**), fluorenone (**4**), *p*-chloranil (**5**), 2,4,6-triphenylpyrylium tetrafluoroborate (**6**)

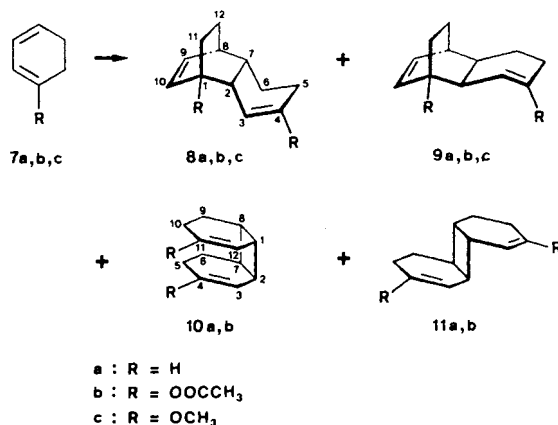


Figure 3. Cyclodimerizations of 1,3-cyclohexadiene (**7a**), 1-acetoxy-1,3-cyclohexadiene (**7b**), and 1-methoxy-1,3-cyclohexadiene (**7c**) to Diels-Alder dimers **8a**, **b**, **c** and **9a**, **b**, **c**, and cyclobutane dimers **10a**, **b** and **11a**, **b**

tion of **7a** in the presence of several electron acceptors, especially ketone/LiClO₄ mixtures^{52–54}.

In this work new preparative and mechanistic studies on the radical-cation dimerization of **7a** will be presented⁵⁶.

The dimerization of **7a** has been carried out in presence of several electron acceptors (see Figure 2) at different concentrations of the diene **7a** (see Table 1 and Figures 3 and 4).

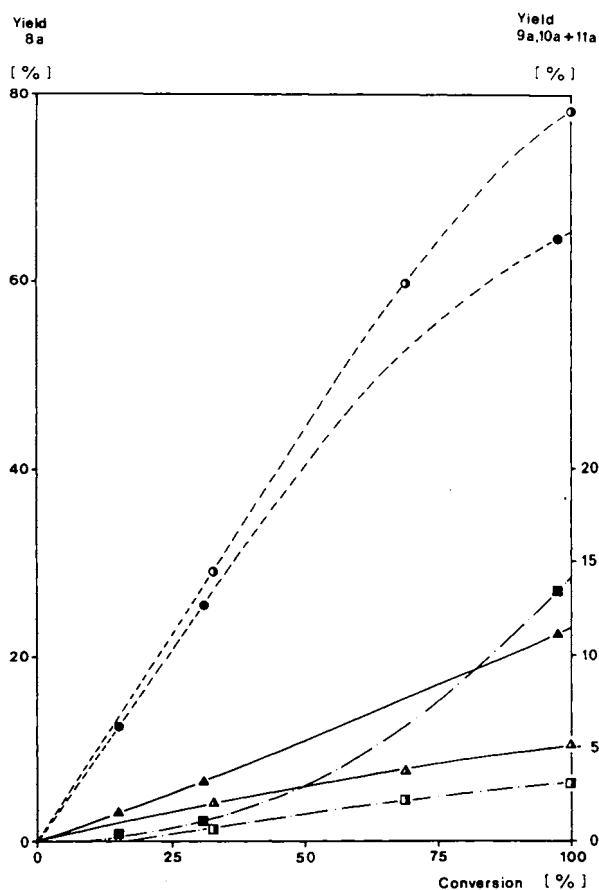


Figure 4. Cyclodimerization of **7a** at two different concentrations of **7a** in the presence of **2** (0.02 M) as electron acceptor in acetonitrile: product yield versus conversion of **7a** (full symbols: 0.4 M **7a**, half symbols: 0.1 M **7a**). Products: ●, ○ = **8a**; ▲, △ = **9a**; ■, □ = **10a + 11a**)

The results shown in Table 1 reveal the influence of the diene concentration on the product ratio **8a/9a** – almost independent of the conversion (see Fig. 4). At low concentrations of **7a** in the presence of **2**, **5**, and **6** as electron acceptors, the *endo* dimer **8a** is preferably formed, whereas as higher concentrations of **7a** the *exo* dimer **9a** is favored (see Table 1).

Cyclodimerization of **7a** under electron-transfer conditions in the absence and presence of 1,2,4-trimethoxybenzene (TMB) as electron-transfer quencher or ethanol (EtOH) as nucleophilic scavenger, indicates the involvement of radical-ion intermediates. The formation of Diels-Alder products **8a** and **9a** in the presence of **2**, **5**, or **6** as electron acceptors is effectively quenched by TMB and EtOH, respectively. In the **2**-sensitized reaction the *endo* dimer **8a** is more effec-

Table 1. Cyclodimerization of **7a** under electron-transfer conditions at different concentrations (conc.) of **7a**

Sens ^{a)}	Conc. [M] 7a	Yield [%] (^{b)}) 8a	Yield [%] (^{b)}) 9a	Yield [%] (^{b)}) 10a + 11a	Ratio 8a/9a
2 ^{c)}	0.1	29.0(88)	2.1 (6)	0.7(2)	14/1
	0.4 ^{d)}	12.5(83)	1.6(11)	0.5(3)	8/1
	2.0	4.1(82)	0.6(12)	0.2(4)	7/1
5 ^{e)}	0.05 ^{f)}	44.0(63)	1.8 (3)	–	24/1
	0.1 ^{g)}	39.8(72)	2.6 (5)	–	15/1
	0.4 ^{d)}	17.3(86)	2.0(10)	–	9/1
	1.0	7.9(82)	1.1(12)	0.1(1)	7/1
6 ^{h)}	0.05	16.1(89)	1.7 (9)	–	10/1
	0.1	21.2(85)	3.0(12)	–	7/1
	0.2	8.0(80)	1.5(15)	–	5/1
	0.4	18.5(79)	4.0(17)	–	5/1
	1.0	2.3(77)	0.6(20)	–	4/1

a) Sens = Sensitizer. – ^{b)} (%): Yield with regard to conversion of **7a**. All yields have been determined by GC using naphthalene as internal standard for products and toluene for the diene **7a**. – ^{c)} 0.02 M **2**, CH₃CN, λ ≥ 300 nm, t = 90 min. – ^{d)} In presence of salt (0.2 M LiClO₄) only a very slight influence on the product ratio **8a/9a** in favour of the *endo* dimer **8a** has been observed. – ^{e)} 0.02 M **5**, CH₃CN, λ ≥ 350 nm, t = 60–90 min. In additional experiments for dimerization of **7a**, the concentration of **5** has been reduced: 0.05 M **7a**, 0.0025 M **5**: ratio **8a/9a** = 22/1; 0.1 M **7a**, 0.005 M **5**: ratio **8a/9a** = 15/1. In these cases dehydrated dimers of **7a** have not been observed. – ^{f)} 8% of a dehydrated dimer of **7a** (molar mass = 156) and benzene have been found. Yield with regard to conversion of **7a** has been determined within a tolerance of about 5%. – ^{g)} 3.7% of the dehydrated dimer (see note f)). – ^{h)} 0.004 M **6**, CH₂Cl₂, λ ≥ 350 nm, t = 10–30 min.

Table 2. Cyclodimerization of **7a** under electron-transfer conditions in the absence and presence of 1,2,4-trimethoxybenzene (TMB) as electron-transfer quencher or ethanol (EtOH) as nucleophilic scavenger

Sens ^{a)}	7a	Conc. [M] TMB	Conc. [M] EtOH	Yield [%] (^{b)}) 8a	Yield [%] (^{b)}) 9a
2 ^{c)}	0.2	–	–	7.0	0.8
	0.2	0.02	–	1.3(81)	0.4(50)
5 ^{d)}	0.4	–	–	14.6	1.7
	0.4	0.02	–	5.0(66)	0.6(65)
5 ^{d)}	0.4	–	–	17.3	2.0
	0.4	0.1	–	0.9(95)	0.1(95)
5 ^{d)}	0.4	–	–	16.2	1.7
	0.4	–	0.4	2.9(82)	0.3(82)
6 ^{e)}	0.1	–	–	21.2	3.0
	0.1	0.02	–	3.5(83)	0.6(80)

a, b) See notes a, b) of Table 1. In the presence of TMB or EtOH, the small conversion of **7a** corresponds with the low yields. A consumption of TMB has not been observed. – ^{c)} 0.02 M **2**, CH₃CN, λ ≥ 300 nm, t = 30 min. – ^{d)} 0.02 M **5**, CH₃CN, λ ≥ 350 nm, t = 40 min. – ^{e)} 0.004 M **6**, CH₂Cl₂, λ ≥ 300 nm, t = 15 min.

tively quenched by TMB than the *exo* dimer **9a** (see Table 2).

2.1.2. 1-Acetoxy-1,3-cyclohexadiene (**7b**)

The radical-cation Diels-Alder dimerization of **7b** initiated by singlet excited **6** was described first by Steckhan⁶¹⁾ (**8b + 9b**: 25%, **8b/9b**: 6/1).

Cyclodimerization of **7b** under electron-transfer conditions using **1**, **2**, **4**, or **5** as electron acceptor gives Diels-Alder dimers **8b** and **9b** in good yields (see Figure 3 and Table 3). Cyclobutane products **10b** and **11b** are formed if **2** or **4** are used as electron acceptor and in presence of **5** at longer reaction times. Variation of the diene concentration in the dimerization sensitized by 1,4-dicyanonaphthalene (**2**) reveals a dependency of the product ratio on the concentration of the diene that is comparable with the results obtained in the corresponding reaction of **7a** (see Tables 1 and 3). At low concentrations of **7b** the *endo* dimer **8b** is favored, at higher concentrations of **7b** the *exo* dimer **9b** is preferably formed (see Table 3). Furthermore, high concentrations of **7b** favor the formation of cyclobutane dimers **10b** and **11b** if **2** is used as acceptor (see Table 3). Quenching experiments with TMB and EtOH indicate the involvement of radical-ion intermediates in the cyclobutane formation here (see Table 4 and Figure 5). The formation of Diels-Alder products **8b** and **9b** is effectively quenched in all cases (see Table 4).

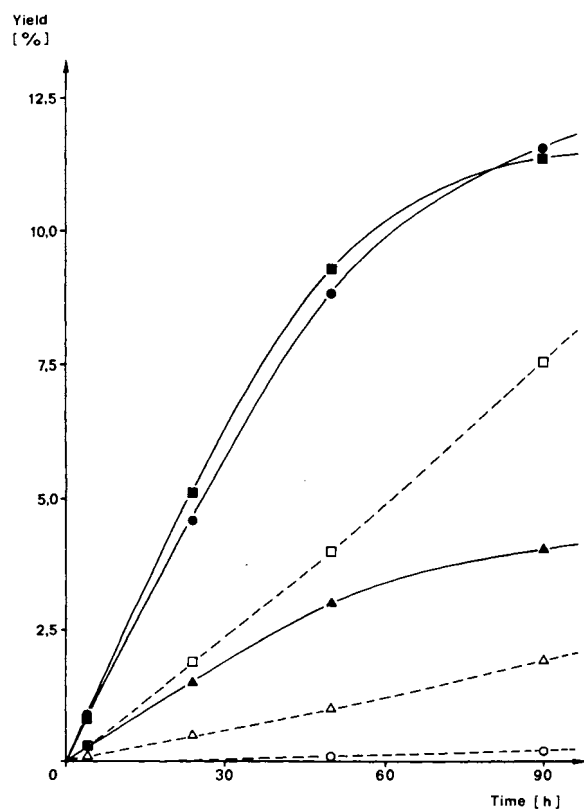


Figure 5. Cyclodimerization of **7b** (0.2 M) sensitized by **2** in CH_3CN in the absence and presence of 1,2,4-trimethoxybenzene (TMB) (0.02 M) as electron-transfer quencher (full symbols: absence of TMB, open symbols: presence of TMB; Products: ●, ○ = **8b**; ▲, △ = **9b**; ■, □ = **10b** + **11b**)

2.1.3. 1-Methoxy-1,3-cyclohexadiene (**7c**)

The electron-transfer Diels-Alder dimerization of **7c** (see Figure 3) was described first by Bauld^{63,64} who used 1,4-dicyanobenzene (**3**) as electron acceptor. Later Steckhan⁶¹ carried out this reaction in the presence of **6** as electron

Table 3. Cyclodimerization of **7b** under electron-transfer conditions at different concentration of **7b**

Sens ^{a)}	Conc. [M] 7b	Yield [% (% ^{b)}]			Ratio [2 + 2] [2 + 4]	
		8b	9b	10b + 11b	8b/9b	
1 ^{c)}	0.4	62	21	—	3/1	—
2 ^{d,e)}	0.05 ^{o)}	8.1	0.9	1.5	9/1	0.2/1
	0.2	0.9(43)	0.3(14)	0.8(38)	3/1	0.7/1
	0.4	2.3(38)	1.0(16)	2.6(43)	2.3/1	0.8/1
2/LiClO₄ ^{d)}	0.4	2.6(46)	1.0(18)	1.8(32)	2.6/1	0.5/1
4/LiClO₄ ^{g)}	0.4	2.5(21)	2.1(18)	4.7(39)	1.2/1	1/1
5 ^{e,h)}	0.3	10.0(87)	1.0(9)	—	10/1	—
6 ⁱ⁾	0.05 ^{j)}	12.9	2.2	—	5.9/1	—
	0.3 ^{k)}	17.7	3.2	—	5.5/1	—

^{a)} Sens = Sensitizer. — ^{b)} (%): Yield with regard to conversion of **7b**. All yields have been determined by GC using phenanthrene as internal standard for the products and toluene for the diene **7b**. At longer reaction times, traces of other, not identified dimers of **7b** have been observed aside from the products **8b**–**11b**. — ^{c)} 0.02 M **1**, CH_2Cl_2 , $t = 20$ min. — ^{d)} 0.02 M **2** (0.2 M LiClO_4), CH_3CN , $\lambda \geq 300$ nm, $t = 4$ – 22 h. — ^{e)} If the dimerization of **7b** with **2** or **5** as sensitizer is carried out in benzene the *exo* dimer **9b**, the cyclobutane dimers **10b** and **11b**, as well as traces of other dimers of **7b** have been observed. The *endo* dimer **8b** has not been found. — ^{f)} Yield [%] after 44 h: **8b**: 14.7(42), **9b**: 1.5(4), **10b** + **11b**: 2.6(7). — ^{g)} 0.05 M **4**, 0.2 M LiClO_4 , CH_3CN , $\lambda \geq 350$ nm, $t = 6$ d. — ^{h)} 0.02 M **5**, CH_3CN , $\lambda \geq 350$ nm, $t = 25$ min. In the presence of LiClO_4 (0.2 M), the same result has been obtained. — ⁱ⁾ 0.004 M **6**, CH_2Cl_2 , $\lambda \geq 350$ nm. — ^{j)} $t = 0.5$ h; yield [%] after 5 h: **8b**: 40.4(59), **9b**: 7.2(11). — ^{k)} $t = 5$ h; yield [%] after 44 h: **8b**: 50.7(67), **9b**: 10.2(13).

Table 4. Cyclodimerization of **7b** under electron-transfer and triplet conditions in the absence and presence of 1,2,4-trimethoxybenzene (TMB) as electron-transfer quencher or ethanol (EtOH) as nucleophilic scavenger

Sens ^{a)}	7b	Conc. [M]		Yield [%] ^{b)} (Quenching [%])			
		TMB	EtOH	8b	9b	10b	11b
2 ^{c)}	0.2	—	—	4.6	1.5	1.3	3.8
	0.2	0.02	—	— (100)	0.5(67)	0.4(69)	1.5(61)
	0.2	—	0.8	0.5 (89)	0.6(60)	0.6(54)	1.7(55)
5 ^{d)}	0.5	—	—	2.5	0.4	—	—
	0.5	0.02	—	— (100)	— (100)	—	—
6 ^{e)}	0.3	—	—	17.7	3.2	—	—
	0.3	0.02	—	0.4 (98)	0.1(97)	—	—
Acph ^{f)}	0.3	—	—	—	2.3	1.8	6.4
	0.3	—	1.2	—	2.2	1.8	6.3

^{a,b)} See notes^{a,b)} of Table 3. — ^{c)} 0.02 M **2**, CH_3CN , $\lambda \geq 300$ nm, $t = 24$ h. — ^{d)} 0.015 M **5**, CH_3CN , $\lambda \geq 350$ nm, $t = 20$ min. — ^{e)} 0.004 M **6**, CH_2Cl_2 , $\lambda \geq 350$ nm, $t = 5$ h. — ^{f)} 0.03 M acetophenone (Acph), C_6H_6 , $\lambda \geq 300$ nm, $t = 24$ h; traces of other dimers of **7b** have been found as well.

acceptor and isolated the Diels-Alder dimers **8c** and **9c** in their hydrolyzed forms.

In this work, **2** and **4** combined with LiClO_4 have been used as efficient sensitizers for the Diels-Alder dimerization of **7c** (see Table 5). The products **8c** and **9c** were obtained in high yields; cyclobutane dimers were not found under electron-transfer conditions. Using **2** as electron acceptor, an evident salt effect could be demonstrated: In the presence of LiClO_4 the reaction rate for the dimerization of **7c** was six times higher than in the absence of salt. Furthermore, the consumption of the sensitizer was suppressed by addition of LiClO_4 .

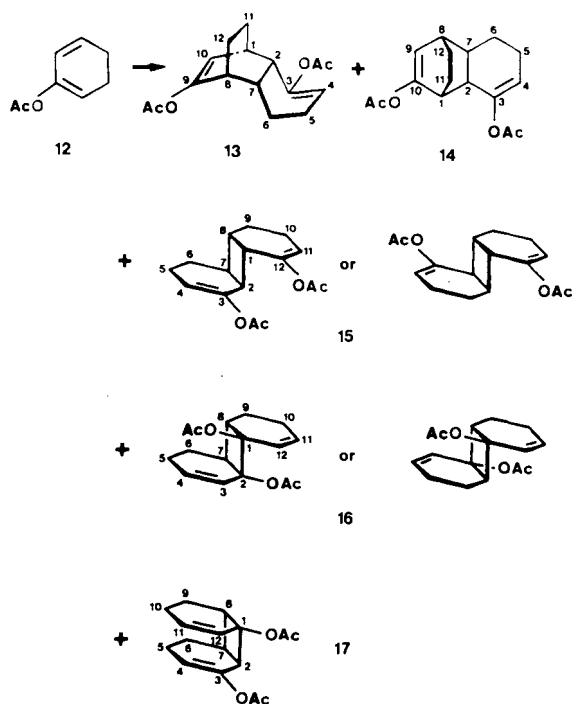
Table 5. Cyclodimerization of **7c**^{a)} under electron-transfer and triplet conditions

Sensitizer	Yield [% (% ^{b)}] 8c + 9c	Ratio ^{c)} 8c/9c
2 ^{d)}	12(99)	1.6/1
2 /LiClO ₄ ^{d)}	73(99)	1.6/1
3 ^{e)}	44(99)	1.6/1
4 /LiClO ₄ ^{f)}	94(99)	1.6/1
Acph ^{g)}	—	—

^{a)} A mixture of 1,3- and 1,4-diene (80/20) has been used. Conversion of the 1,4-diene has not been observed. — ^{b)} (%): Yield with regard to conversion of **7c**. All yields have been determined by GC using biphenyl as internal standard for the products and toluene for the diene **7c**. — ^{c)} The ratios have been determined within a tolerance of about 12%. — ^{d)} 0.4 M **7c**, 0.02 M **2** (0.2 M LiClO₄), CH₃CN, λ ≥ 300 nm, t = 15 h. In the absence of salt: 35% consumption of **2**; in the presence of salt: 19% consumption of **2**. Adducts between **2** and **7c** have not been observed. — ^{e)} 0.5 M **7c**, 0.18 M **3**, CH₃CN, λ ≥ 300 nm (conditions as described by Bauld^{63,64}); **3** was not quantitatively dissolved, t = 3 d. — ^{f)} 0.75 M **7c**, 0.05 M **4**, 0.2 M LiClO₄, CH₃CN, λ ≥ 350 nm, t = 1 d. — ^{g)} 0.4 M **7c**, 0.1 M acetophenone (Acph), C₆H₆, λ ≥ 300 nm, t = 3 d; six not identified dimers (total 20%, conversion of **7c**: 22%) and anisole have been found.

2.1.4. 2-Acetoxy-1,3-cyclohexadiene (**12**)

Cyclodimerization of **12** under electron-transfer conditions is as unselective as the triplet-sensitized dimerization of **12**. All the products **13**–**17** shown in Figure 6 have been isolated. There is no significant quenching effect on the product formation using TMB as electron-transfer quencher in the presence of **2** or **4** as sensitizer.

Figure 6. Cyclodimerization of 2-acetoxy-1,3-cyclohexadiene (**12**) to Diels-Alder products **13** and **14**, and cyclobutane dimers **15**–**17**Table 6. Cyclodimerization of **12** under electron-transfer and triplet conditions

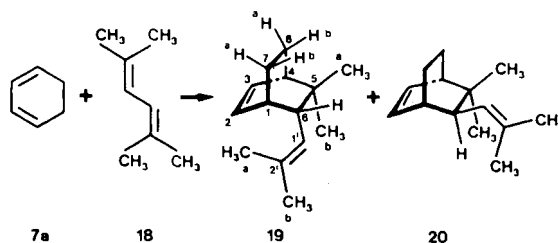
Sensitizer	Yield [% (% ^{a)}] 13 + 15 14 16			17	Others ^{b)}
2 ^{c)}	20.0(36)	3.4(6)	3.9(7)	14.3(26)	7.6(14)
2 /LiClO ₄ ^{c)}	17.7(48)	4.1(11)	0.9(2)	1.8(5)	4.9(13)
4 /LiClO ₄ ^{d)}	3.7(62)	1.0(17)	^{e)}	^{e)}	0.8(13)
Acph ^{f)}	41.2(43)	9.1(10)	5.7(6)	17.1(18)	4.0(4)

^{a)} (%): Yield with regard to conversion of **12**. All yields have been determined by GC using bibenzyl as internal standard for the products and naphthalene for the diene **12**. — ^{b)} Unidentified dimers. Furthermore the formation of phenyl acetate has been observed. — ^{c)} 0.4 M **12**, 0.02 M **2** (0.2 M LiClO₄), CH₃CN, λ ≥ 300 nm, t = 41 h. In the presence of 0.2 M 1,2,4-trimethoxybenzene (TMB), the max. product quenching was 40%. — ^{d)} 0.4 M **12**, 0.02 M **4**, 0.2 M LiClO₄, CH₃CN, λ ≥ 350 nm, t = 41 h. In the presence of 0.02 M TMB, product quenching was insignificant. — ^{e)} Total λ ≤ 0.5%.

2.2. Crossed Cycloadditions

2.2.1. 1,3-Cyclohexadiene (**7a**) and Electron-Rich Olefins

The radical-cation Diels-Alder reaction between **7a** and 2,5-dimethyl-2,4-hexadiene (**18**) has been carried out by Bauld^{63,64} in the presence of **1** and by Steckhan⁶¹ in the presence of **6** as electron acceptor. Along with dimers of **7a** (**8a** and **9a**), the Diels-Alder products **19** and **20** were obtained in both cases with a high *endo* selectivity and in good yields (**19** + **20**: 61.3%^{63,64}, 39%⁶¹); **19/20**: 4/3^{63,64}, 5/3⁶¹); see Figure 7). Jones used 9,10-dicyanoanthracene as electron acceptor but she obtained neither crossed Diels-Alder adducts nor dimers of **7a**⁵⁹).

Figure 7. Diels-Alder reaction of **7a** and 2,5-dimethyl-2,4-hexadiene (**18**)

In this work, **1** and **6** as well as the electron-transfer sensitizers **2** and **4** combined with LiClO₄ were used for the Diels-Alder reaction of **7a** and **18** (see Table 7a). The results indicate the involvement of deactivating processes within the photo-induced reaction.

Despite long reaction times, not only the products **19** and **20** but also the Diels-Alder dimers of **7a** were obtained only in poor absolute yields. At longer reaction times, dimers of **7a** could be observed in better yields but the isomer ratios were very similar to those obtained under triplet conditions.

The formation of **19** and **20** was significantly quenched when TMB ($E_{1/2}^{ox} = 0.82$ V)⁶⁵ was used as electron-transfer quencher, whereas 1,4-dimethoxybenzene (DMB) ($E_{1/2}^{ox} = 1.04$ V)⁶⁵ did not show any quenching effect [$E_{1/2}^{ox}(\mathbf{7a}) = 1.15$ V⁶⁶], $E_{1/2}^{ox}(\mathbf{18}) = 0.91$ V] (see Table 7b).

Similar results were obtained in the radical-cation Diels-Alder reaction between **7a** and 1,4-dioxene (**21**). While the

Diels-Alder products **22a** and **23a** (see Figure 8) were isolated in moderate yields in the presence of **1** and **6** as electron acceptors, product formation was significantly inhibited if **2**, **4**, or **5** were used as electron-transfer sensitizers (see Table 8).

Table 7. Diels-Alder reaction of **7a** and **18** (a) under electron-transfer conditions and (b) under electron-transfer conditions in the absence and presence of 1,2,4-trimethoxybenzene (TMB) and 1,4-dimethoxybenzene (DMB) as electron-transfer quenchers

Ratio ^{a)} 7a/18	Sens ^{b)}	Yield [% (% ^{c)}]			Ratio	
		19+20	8a+9a	10a+11a	19/20	8a/9a
0.5/0.5	1 ^{d)}	32	27	—	1.3/1	5/1
0.2/1.0	1 ^{d)}	80	9	—	1.3/1	5/1
0.2/1.0	2 ^{e)}	0.7(27)	0.9(35)	0.9(35)	—	2/1
0.2/1.0	2/LiClO ₄ ^{e)}	2.4(53)	1.6(36)	0.4(9)	2.0/1	4.3/1
0.2/1.0	4/LiClO ₄ ^{f)}	2.0(50)	1.1(28)	0.4(10)	2.3/1	2.7/1

Ratio ^{a)} 7a/18	Sens ^{b)} , Q ^{b)}	Yield [% ^{c)} (Quenching [%])	
		19+20	8a+9a
0.1/0.1	4/LiClO ₄ ^{g)}	2.3	0.8
0.1/0.1	4/LiClO ₄ /TMB ^{g)}	0.5(80)	—
0.1/1.0	4/LiClO ₄ /TMB ^{g)}	2.3	0.8

^{a)} Ratio in M/M. — ^{b)} Sens = Sensitizer, Q = Quencher. — ^{c)} (%): Yield with regard to conversion of **7a**. All yields have been determined by GC using biphenyl as internal standard for the products and toluene for the starting materials. In the photochemical experiments, the conversion of **18** corresponds with the yield of **19** and **20**. — ^{d)} 0.025 M **1**, CH₂Cl₂, t = 15 min; when the ratio **7a/18** was 1/5, also 11% of (*endo*-2,*exo*-3,*exo*-6)-1,2,4,4-tetramethyl-3-(2'-propenyl)-6-(2'-propyl)bicyclo[3.1.0]hexane and 4% of other dimers and trimers of **18** have been found (see ref. ⁶⁷⁾). — ^{e)} 0.01 M **2** (0.2 M LiClO₄), CH₃CN, λ ≥ 300 nm, t = 1 d. — ^{f)} 0.05 M **4**, 0.2 M LiClO₄, CH₃CN, λ ≥ 350 nm, t = 1 d. — ^{g)} 0.02 M **4**, 0.2 M LiClO₄ (0.02 M TMB, DMB), CH₃CN, λ ≥ 350 nm, t = 1 d.

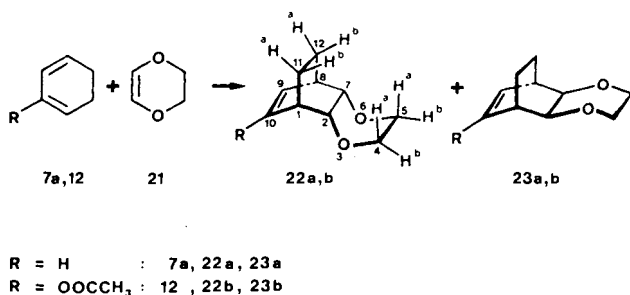


Figure 8. Diels-Alder reaction between **7a** and 1,4-dioxene (**21**) and between **12** and **21**, respectively

2.2.2. Substituted 1,3-Cyclohexadienes (**7b**, **7c** and **12**) and 1,4-Dioxene (**21**)

Experiments concerning the radical-cation Diels-Alder reaction of **7b** and **21** (tenfold excess of **21**) in the presence of **2**, **4**, or **5** as electron-transfer sensitizer (in acetonitrile), yielded only traces of dimers of **7b** and no other products. Using **1** or **6** as electron acceptor in this reaction two 1/1-

Table 8. Diels-Alder reaction of **7a** and **21** under electron-transfer conditions and in the presence of acetophenone (Acph) as triplet sensitizer

Ratio ^{a)} 7a/21	Sensitizer	Yield [% (% ^{b)}]		Ratio ^{c)}	
		22a+23a	Dimers of 7a ^{d)}	22a/23a	8a+9a/10a+11a
0.1/1.0	1 ^{e)}	23	3	1.6/1	—
0.16/0.08	1 ^{e)}	29	39	2.3/1	—
0.05/0.5	2 ^{f)}	0.1 (2)	5.2(87)	g)	0.4/1
0.05/0.5	2/LiClO ₄ ^{g)}	0.3 (7)	3.9(91)	g)	0.7/1
0.05/0.5	4/LiClO ₄ ^{h)}	0.4(20)	0.5(25)	g)	0.5/1
0.05/0.5	5 ⁱ⁾	0.8 (5)	13.2(78)	g)	0.9/1
0.05/0.5	5/LiClO ₄ ⁱ⁾	2.7(64)	0.8(19)	g)	g)
0.05/0.5	6 ^{j)}	14 (35)	24 (60)	8/1	17/1
0.05/0.5	Acph ^{k)}	—	95	—	0.3/1

^{a)} Ratio M/M. — ^{b)} (%): Yield with regard to conversion of **7a**. All yields have been determined by GC using naphthalene as internal standard for the products and toluene for the starting materials. In the photochemical experiments, the conversion of **21** corresponds with the yield of **22a** and **23a**. — ^{c)} Ratio **8a+9a/10a+11a** within a tolerance of ca. 10%. — ^{d)} Products **8a–11a**. — ^{e)} 20 mol % **1** related to concentration of **7a**, CH₂Cl₂, t = 20 min. — ^{f)} 0.01 M **2** (0.2 M LiClO₄), CH₃CN, λ ≥ 300 nm, t = 1 d. — ^{g)} Only *endo*-[2+4] product has been observed. — ^{h)} 0.025 M **4**, 0.2 M LiClO₄, CH₃CN, λ ≥ 350 nm, t = 1 d. — ⁱ⁾ 0.0075 M **5** (0.075 M LiClO₄), CH₃CN, λ ≥ 350 nm, t = 1 d. Similar results at higher concentrations of **5** and LiClO₄. — ^{j)} 0.0015 M **6**, CH₂Cl₂, λ ≥ 350 nm, t = 1 d. — ^{k)} 0.04 M Acph, C₆H₆, λ ≥ 300 nm, t = 1 d.

Table 9. Diels-Alder reaction of **12** and **21** (a) under electron-transfer conditions and (b) under electron-transfer conditions in the absence and presence of 1,2,4-trimethoxybenzene (TMB)

Ratio ^{a)} 12/21	Sensitizer	Yield [% (% ^{b)}]		Ratio 22b/23b
		22b+23b	22b/23b	
0.1/1.0	1 ^{c)}	31	1.5/1	1.5/1
0.1/1.0	4/LiClO ₄ ^{d)}	12(80)	0.7/1	0.7/1
0.05/0.5	4/LiClO ₄ ^{e)}	30(81)	1/1	1/1
0.05/0.5	5/LiClO ₄ ^{f)}	15(83)	1/1	1/1
0.05/0.5	6 ^{g)}	40(80)	0.7/1	0.7/1

Ratio ^{a)} 12/21	Sensitizer, Quencher	Yield [% ^{b)} (Quenching [%])	
		22b	3b
0.1/1.0	5 ^{h)}	1.5	1.3
0.1/1.0	5/TMB ^{h)}	≤0.1 (≥93)	≤0.1 (≥92)
0.1/1.0	5/LiClO ₄ ^{h)}	6.6	4.7
0.1/1.0	5/LiClO ₄ /TMB ^{h)}	1.3(80)	1.1(77)
0.05/0.5	6 ⁱ⁾	5.6	7.3
0.05/0.5	6/TMB ⁱ⁾	≤0.1 (≥98)	≤0.1 (≥99)

^{a)} Ratio in M/M. — ^{b)} (%): Yield with regard to conversion of **12**. All yields have been determined by GC using biphenyl as internal standard for the products and naphthalene for the diene **12**. — ^{c)} 0.015 M **1**, CH₂Cl₂, t = 30 min. — ^{d)} 0.05 M **4**, 0.2 M LiClO₄ (not quantitatively dissolved), CH₂Cl₂, λ ≥ 350 nm, t = 2 d. The reaction has been carried out also in CH₃CN (**22b/23b** = 1.4/1). In both cases, dimers of **12** (**13–17**) have been observed in low yields. — ^{e)} 0.02 M **4**, 0.2 M LiClO₄, CH₃CN. — ^{f)} 0.02 M **5**, 0.2 M LiClO₄, CH₃CN. — ^{g)} 0.004 M **6**, CH₂Cl₂. — ^{h)} 0.02 M **5** (0.2 M LiClO₄, 0.02 M TMB), CH₃CN. — ⁱ⁾ ^{h)} λ ≥ 350 nm, t = 16 h. — ^{j)} 0.004 M **6** (0.01 M TMB), CH₂Cl₂, λ ≥ 350 nm, t = 4 h.

adducts of **7b** and **21** were formed in low yields along with dimers of **7b** (**8b** and **9b**) according to GC-MS analysis. If the reaction sensitized by **6** was carried out with an excess of **7b** (**7b/21**: 0.4 M/0.1 M), the yields of both, **8b** and **9b** as well as of the 1/1 adducts were higher than in the reaction with an olefin excess (**7b/21**: 1/10 → 1/1 adducts < 1%; **7b/21**: 4/1 → 1/1 adducts 3%).

Irradiation of the system **7c/21** (fivefold excess of **21**) with **2/LiClO₄** or **4/LiClO₄** as electron acceptor in acetonitrile gave dimers of **7c** (**8c** and **9c**) in yields as obtained in the corresponding cyclodimerizations of **7c** (see Table 5). Crossed Diels-Alder products of **7c** and **21** were not observed.

Contrary to these results, the crossed Diels-Alder products **22b** and **23b** were formed in good yields if **12** and **21** were irradiated in the presence of **4**, **5**, or **6** as electron acceptor. The ammonium salt **1** also catalyzes the Diels-Alder reaction of **12** and **21** (see Figure 8 and Table 9a). A tenfold excess of the olefin component almost completely inhibited the dimerization of **12**. The formation of **22b** and **23b** could effectively be quenched by TMB (see Table 9b).

2.3. Mechanistic Studies

2.3.1. Cyclodimerizations

A significant dependence of the diene concentration on the product ratio indicates the involvement of different radical-ion intermediates in the radical-cation dimerizations of **7a** and **7b**, respectively (see Tables 1 and 3). While in the dimerizations of **7a** with **2**, **5**, or **6** as electron acceptor only the *endo/exo* ratio **8a/9a** was influenced, we could observe effects both, on the *endo/exo* ratio **8b/9b** and on the formation of cyclobutane dimers **10b** and **11b** in the dimerization of **7b** sensitized by **2**. These cyclobutane adducts could be quenched by TMB and by EtOH. Noteworthy is the different efficiency of quenching the *endo* dimers **8a** and **8b** on the one hand and of the *exo* and cyclobutane dimers **9a**, **9b** and **10b**, **11b** on the other hand if **2** was used as electron acceptor. In the case of **5** and **6** as electron acceptor in the dimerizations of **7a** and **7b**, the quenching of both, *endo*- and *exo*-product formation was nearly the same (see Tables 2 and 4). For a better understanding of the quenching experiments, some kinetic aspects will be discussed here.

Electron-transfer sensitized reactions may be influenced by a quencher in different ways (see Figure 9).

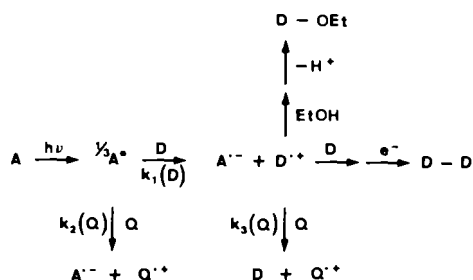


Figure 9. Influence of an electron-transfer quencher (Q) and a nucleophilic scavenger⁶⁸⁾ (EtOH) on electron-transfer-sensitized reactions. Concurrent formation of radical-ion pairs: $k_1(D)$, $k_2(Q)$ (A: acceptor, D: donor, Q: quencher, EtOH: ethanol)

For differentiating between luminescence quenching of the excited acceptor molecule by a quencher molecule (primary electron transfer) on the one hand and reduction of a donor radical cation by a quencher molecule (secondary electron transfer) on the other hand, we have first measured the rates $k_1(D)$ and $k_2(Q)$ for quenching the fluorescence of **12*** by several dienes (**7a**, **b**, and **12**) and by TMB (see Table 10).

Table 10. Stern-Volmer data for quenching of the fluorescence^{a)} of 1,4-dicyanonaphthalene (**2**) by several donor molecules in acetonitrile

Donor	7a	7b	12	TMB
$k_q \times 10^{10}$ [l mol ⁻¹ s ⁻¹]	1.7 ^{b)}	1.3	1.6	2.1

^{a)} τ_0 [**12***(CH₃CN)] = 8.911 ± 0.027 ns⁶⁹⁾. — ^{b)} Calculated with $k_q \cdot \tau_0 = 148$ l mol⁻¹ s⁶⁰⁾.

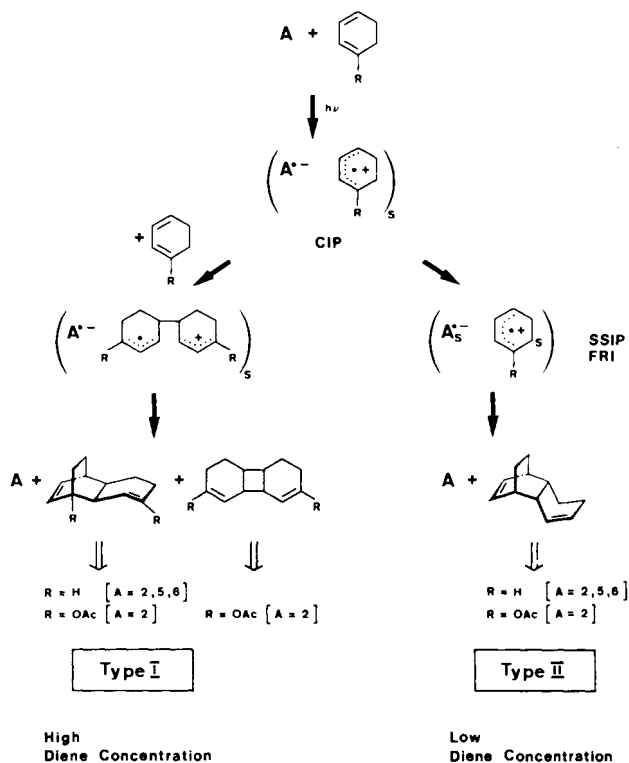


Figure 10. Electron-transfer-sensitized cyclodimerizations of **7a** and **7b** via contact-ion pairs (exciplexes) (I) or via solvated radical ions (II)

Since all values are near the diffusion-controlled limit [$k_{diff}(\text{CH}_3\text{CN}, 20^\circ\text{C}) = 1.86 \times 10^{10}$ l mol⁻¹ s⁻¹]⁷⁰⁾, both quenching processes characterized by $k_1(D)$ and $k_2(Q)$ should proceed with the same efficiency. If Q only affects the first step of the proposed reaction scheme we should observe a quenching effect of max. 10% (quencher/diene = 1/10) on the product formation. However, the product quenching is much more efficient, indicating the involvement of radical-ion intermediates within the dimerizations of **7a** and **7b** sensitized by **2**. It should be mentioned here that

ground-state interactions between donor and acceptor molecules cannot be ruled out, although **7a** and **5**, for example, gave no evidence of a charge-transfer complex⁶⁹. In addition, the product formation was inhibited by EtOH as nucleophilic scavenger in the presence of **2** and **5** as electron acceptors (see Table 2 and 4). Both, the concentration effects and the results of the quenching experiments indicate the involvement of differently solvated radical-ion pairs. The mechanism shown in Figure 10 may rationalize these observations.

At high concentrations, the contact ion pair (CIP), which is formed after the initial electron transfer from the diene **7a** to excited **2**, **5**, or **6**, is quenched by a second molecule of **7a** and leads to the *exo* dimer **9a**. In the case of diene **7b** the CIP yields the *exo* dimer **9b** and the cyclobutane adducts **10b** and **11b** if **2** is used as electron acceptor. Dissoziation into solvent-separated ion pairs (SSIP) occurs at low concentrations of **7a** and **7b** and leads almost quantitatively to the *endo* dimers **8a** and **8b**, respectively. Similar effects have been observed by Farid⁷¹ who described different intermediates in the dimerization of 1,1-diphenylethene with 9,10-dicyanoanthracene as electron acceptor. The formation of differently solvated radical-ion pairs is also influenced by LiClO₄ added to the solution of **7b** and **2** in acetonitrile: The presence of salt favors the formation of the *endo* dimer **8b**, whereas the formation of the *exo* dimer **9b** and of the cyclobutane adducts **10b** and **11b** is suppressed. The results correspond to a study upon pressure and solvent effects on the photochemically induced dimerization of **7a** reported by Mattay and Turro⁷²: The *exo* dimer **9a** is favored over the *endo* dimer **8a** at both, high concentrations of **7a** and high pressure (1–2 kbar). On the contrary, high-pressure dimerization of **7a** with **2** in benzene yielded preferably the *endo* dimer **8a** with an unusually large activation volume of –9 to –12 cm³/mol, which to our knowledge is the currently highest value observed in Diels-Alder reactions⁷². The latter result further proves the Diels-Alder dimerization of **7a** by a mechanism involving ternary intermediates/transition states in nonpolar solvents, termed “triplex-mechanism” according to Schuster^{50,60,73} and may be utilized for controlling the diastereoselectivity by high pressure.

2.3.2. Crossed Cycloadditions

Two phenomena concerning photoinduced, crossed radical-cation Diels-Alder reactions should be discussed here in more detail:

(a) Inhibition of product formation in several cases (see Tables 7a, 8 and Chapter 2.2.)

(b) Successful reaction between **12** and **21** (see Table 9)

Deactivating processes must be involved in the photoinduced Diels-Alder reactions between **7a**, **b**, **c** and **18** or **21** with several electron acceptors (see also ref.⁵⁹). Evidence is given by the quantum yields Φ of the reaction between **7a** and **18** sensitized by **6**, which are $\Phi = 8 \times 10^{-3}$ for the formation of **8a** and **9a** and $\Phi = 5 \times 10^{-2}$ for the formation of **19** and **20**. The corresponding dimerization of **7a** runs

with $\Phi = 0.65$, which might indicate participation of a chain mechanism.

According to the quenching experiments in the system **7a/18** (see Table 7b), we would expect this Diels-Alder reaction to proceed via the radical cation of **18** since the formation of **19** and **20** was quenched by TMB and not by DMB (oxidation potentials see Table 11). But deactivating processes by **19** and **21** themselves have to be considered as well in the crossed Diels-Alder reactions. The dimerization of the diene only proceeds as expected with the system **7c/21**, obviously a consequence of the low oxidation potential of **7c**, which hinders quenching of the radical cation of **7c** by **21**. Hence, the involvement of diene-radical cations in these reactions must be taken into consideration as well. Mechanistic studies upon crossed Diels-Alder reactions are in progress.

Table 11. Oxidation potentials of olefin^{a)} and quencher^{a)} molecules (TMB: 1,2,4-trimethoxybenzene, DMB: 1,4-dimethoxybenzene)

Olefin, Quencher	7a	TMB ⁶⁵⁾	21 ⁶⁶⁾	18	7b	DMB ⁶⁵⁾	12	7a
$E_{1/2}^{\text{ox}}$ [V]	0.52	0.82	0.83	0.91	0.98	1.04	1.12	1.15

^{a)} Using the electron acceptors **2–6**, the ΔG_{ET} values according to Weller^{43–45)} are within a range of –45.1 to +9.8 kcal mol⁻¹.

In contrast to previous results, the electron-transfer-sensitized Diels-Alder reaction between **12** and **21** leads to the products **22b** and **23b** in high yields and with high selectivities (see Table 9). Assuming a multistep mechanism, the efficiency of **7b** and **12** in crossed Diels-Alder reactions on the one the side and dimerizations on the other side will be discussed on the basis of the structures **24a–25b** (see Figure 11).

Upon comparison of the carboxonium ion structures of the intermediates **24a** and **24b**, it becomes obvious that the latter one favors the mixed Diels-Alder reaction. But then in the electron-transfer-sensitized dimerizations of **7b** and **12**, respectively, the acetoxy substituent at position 1 of the allylic unit stabilizes the acyclic radical-ion intermediate (**25a**) more efficiently than one in position 2 (**25b**): High yields and selectivities have been observed in the electron-transfer-sensitized dimerization of **7b** to the products **8b–11b** (see Table 3). Also under triplet conditions the products **9b–11b** were obtained with rather high selectivities. These results indicate a stabilizing influence of both, the radical cation and the biradical mechanism on acyclic intermediates in the dimerization of **7b**. On the contrary, the dimerization of **12** yielded a palette of products (**13–17**) without regioselectivity under electron-transfer and triplet conditions as well (see Table 6). The stability of the radical-ion intermediate **25a** can be explained by a withdrawing effect of the acetoxy group which stabilizes more in position 1 than in position 2 of the allylic units. Already the oxidation potentials of the monomers **7b** ($E_{1/2}^{\text{ox}} = 0.98$ V) and **12** ($E_{1/2}^{\text{ox}} = 1.12$ V) indicate such an effect [for comparison: E^{ox} (**7a**) = 1.15 V⁶⁶⁾].

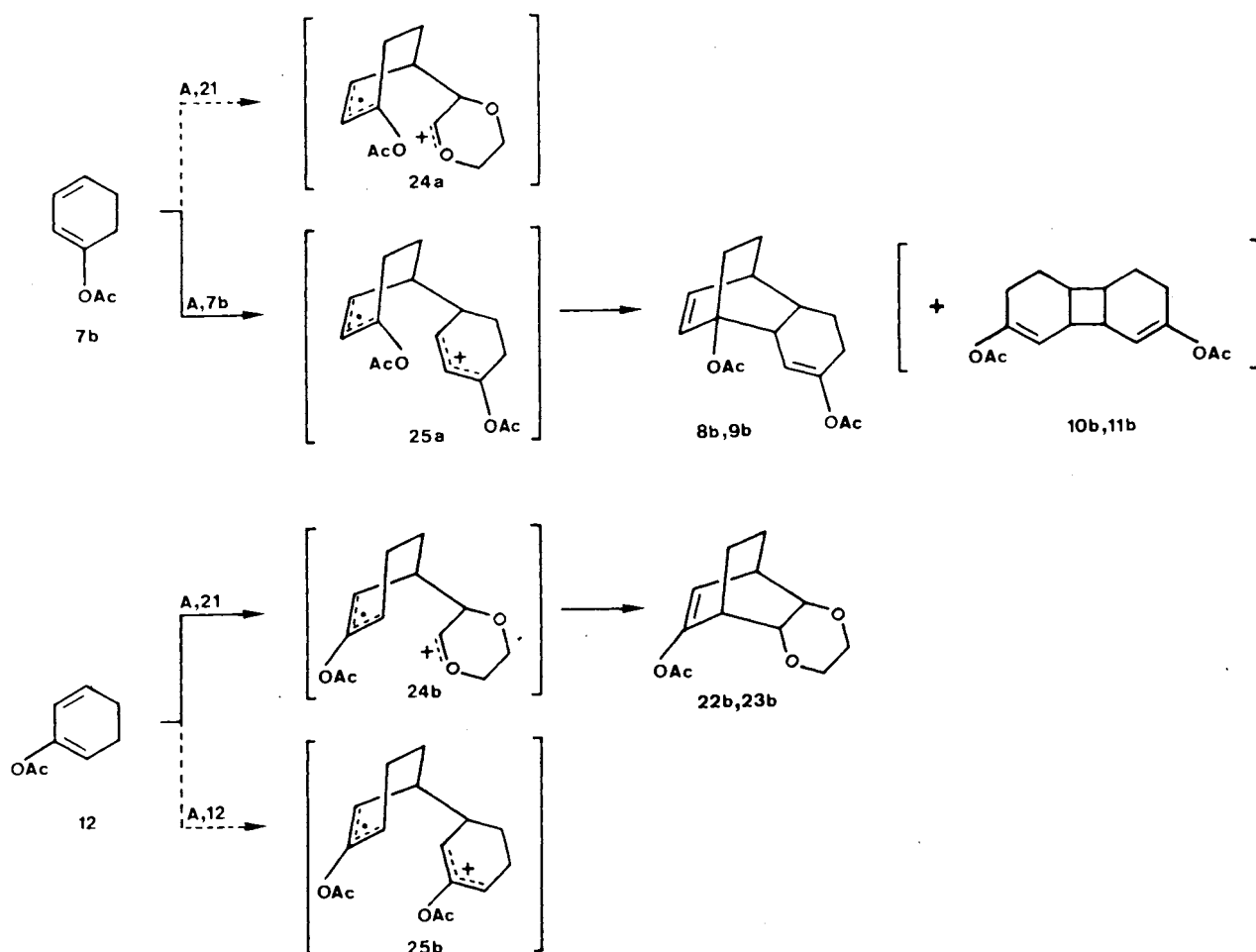


Figure 11. Comparison of dienes **7b** and **12** in cyclodimerizations and crossed Diels-Alder reactions with **21** under electron-transfer conditions (A: acceptor)

2.4. Side Reactions

Especially in the case of multistep-radical-cation cycloadditions side reactions must be considered. Acyclic 1/1 and 1/2 adducts have been observed by Mizuno³²⁾ in the Diels-Alder reaction between furan and indene with 1-cyanonaphthalene as electron acceptor. Besides such substitution reactions, oxidation/reduction processes involving the electron acceptor as oxidizing species have to be considered as well. For example, Farid^{7(b)} described competing [2+2] and [2+4] cyclizations as well as radical-cation/radical-anion interactions resulting in competition between electron transfer and proton transfer, depending on the electron acceptor used. In the dimerization of 1,1-diphenylethene with 9,10-dicyanoanthracene as electron acceptor, an acid-base reaction between the product-radical cation and the sensitizer-radical anion yielded *cis*- and *trans*-dihydrodicyanoanthracene and a dehydrated dimer or 1,1-diphenylethene. Corresponding results have been obtained in this work. Using **5** as electron acceptor in the electron-transfer-sensitized cyclodimerizations, tetrachlorohydroquinone has been identified by GC-MS analysis. In the case of the dimerization of **7a** with **5** as electron acceptor, a dehydrated dimer of **7a** (mol. mass = 156) and benzene have been observed when

the concentration of **5** was 20 mol% or more of the diene concentration. The dimerization of **7b** and **12** with **5** as electron acceptor yielded phenylacetate and the reduced sensitizer as byproducts. Furthermore, radical-cation cycloadditions can be influenced by the involvement of triplet-reaction channels. For example, in the cyclodimerization of **7a** or **7b** with **5** as electron acceptor increasing cyclobutane formation (**10a**, **11a** and **10b**, **11b**, respectively) has been observed at longer reaction times. This cyclobutane formation could be reduced by addition of LiClO₄ or, almost completely, by addition of more sensitizer. Further, the absolute yields of [2+4] dimers (**8a**, **9a** and **8b**, **9b**) could be increased by the addition of more sensitizer. In the dimerization of **7a** with **2** as electron acceptor, we observed the same phenomenon however with less evidence.

These results indicate the involvement of triplet-reaction pathways obviously caused by decomposition of **5** (or **2**) at longer reaction times yielding an effective triplet sensitizer. In addition, recombination of radical ions or deactivation of exciplexes under formation of triplets have to be considered. Finally, protic acid catalysis as described by Gassman¹²⁾ may also cause a Diels-Alder dimerization. The influence of Lewis acids observed in the dimerization of **18**

with **1** as electron acceptor ($\text{SbCl}_6^- \rightleftharpoons \text{SbCl}_5 + \text{Cl}^-$) will be reported in more detail⁶⁷⁾.

Here, controlling experiments using HSbCl_6 were carried out in the dimerization of **7b** and in the crossed Diels-Alder reaction of **7a** with **18** and **21**, respectively. Diels-Alder products and cyclobutane dimers have not been observed. In addition, Diels-Alder products of **7a** and **18** could not be obtained at high-pressure conditions (14 kbar, 50 °C)⁷⁴⁾.

Experiments on the dimerization of **7b** in the presence of AlCl_3 yielded neither Diels-Alder products **8b** and **9b** nor cyclobutane dimers **10b** and **11b**.

2.5. NMR Studies

The stereo- and regiochemistry of all dimer products have been determined as far as possible by NMR analysis including COSY and HECTOR studies and by comparison of the observed ¹H-NMR data with those of **8a**–**11a** reported in the literature⁷⁵⁾ (¹H-NMR data see: Experimental; ¹³C-NMR data see Tables 12 and 13). Some characteristic differences between *endo/exo* as well as *syn/anti* dimers will be discussed here. The ¹³C-NMR signals of all CH and CH₂ groups of the *exo* dimers **9a**, **b**, **c** have been observed at chemical shifts up to 5 ppm lower than the corresponding signals of the *endo* dimers **8a**, **b**, **c** (see Table 13). The stereochemistry of product **14** could not be determined clearly, however the ¹³C-NMR spectrum shows low chemical shifts for the CH and CH₂ groups, which are typical for the *exo* isomer (see Table 13). ¹³C-NMR spectroscopic differences have also been observed for the cyclobutane isomers (**10a**, **b** and **11a**, **b** and **15**; see Table 12). The chemical shifts of the tertiary carbons C-1 and C-7 in the ¹³C-NMR spectra are up to 8 ppm apart in the case of *anti* arrangement of the ring systems, whereas in the case of *syn* arrangement the corresponding differences do not exceed 1.8 ppm. Further-

Table 12. ¹³C-NMR data of the cyclobutane dimers **10a**, **b**, **11a**, **b**, and **15**, **16** (all 75 MHz, C₆D₆)

	10a		11a	
H ₃ C	—	—	—	—
C-6, 9	22.06, 23.46		21.61, 22.33	
C-5, 10				
C-7, 8	35.59		32.22	
C-1, 2	36.07		39.67	
C-3, 12	128.63, 128.71		126.83, 130.46	
C-4, 11				
O=C	—	—	—	—

	10b	11b	15	16
H ₃ C	20.54	20.62	20.66	21.19
C-6, 9	22.72	22.97	21.59	17.69, 21.08
C-5, 10	26.10	24.02	21.35	
C-7, 8	33.92	31.11	34.21	35.60
C-1, 2	35.72	39.46	39.38	80.78
C-3, 12	113.67	116.25	150.22	131.60
C-4, 11	150.66	149.09	114.82	124.96
O=C	168.51	168.59	168.52	168.75

more, models of the molecules reveal a preference of different chair conformations of the six-membered ring in dependency of the stereochemistry of the substrate: In the case of the *syn* isomer an axial position of the proton at C-7 is favored — the ¹H-NMR spectrum shows large coupling constants between 7-H and the neighbouring CH₂ group — whereas in the case of the *anti* isomer the six-membered ring prefers the other chair conformation with 7-H in an equatorial position resulting in smaller coupling constants between 7-H and the CH₂ group (see Experimental). In addition, the structures of the cyclobutane dimers **10b** and **11b** have been verified by thermal rearrangement of the *syn* iso-

Table 13. ¹³C-NMR data of the Diels-Alder dimers **8a**, **b**, **c**, **9a**, **b**, **c**, and **13**, **14** and of the unsymmetrical cyclobutane dimer **17** as well (**8b**, **9b**: 20 MHz, CCl₄/C₆D₆; others: 75 MHz, C₆D₆)

	8a	9a		8b	9b	8c	9c		13	14	17
			H ₃ C	20.51	20.47	49.90	50.29	H ₃ C	20.44	20.42	20.97
				21.56	21.41	53.30	53.50		20.57	20.53	21.62
	23.69	18.67		25.92	21.69	26.08	21.92	C-5	23.70	23.64	21.13 ^{a)}
C-5, 6, 11, 12	25.58	21.36		26.52	23.71	26.84	23.33	C-6	25.69	25.85	19.66
	26.59	25.06	C-5, 6, 11, 12	28.19	26.46	27.41	26.58	C-11	19.82	19.29	131.07
	27.46	26.05		28.43	27.14	28.46	28.22	C-12	22.23	22.73	127.67
	36.75	33.19		36.34	33.31	36.50	34.44	C-1	32.28	36.42	76.89
	37.02	35.32	C-2, 7, 8	37.95	34.46	39.75	34.80	C-2	39.29	38.47	45.25
C-1, 2, 7, 8	39.26	35.72		42.16	38.80	41.53	37.80	C-7	34.39	35.22	28.48
	40.43	36.87	C-1	83.16	81.78	79.92	79.58	C-8	39.79	35.90	39.99
	127.94	130.11	C-3	112.01	111.15	92.43	91.02	C-4	117.59	117.57	116.95
	132.23	131.94		130.38	131.88	131.38	134.26	C-9	150.01	117.84	18.14
C-3, 4, 9, 10	132.98	134.44	C-9, 10	133.82	135.72	134.55	134.66	C-3	156.28	149.65	147.32
	138.68	135.61	C-4	150.86	151.64	157.57	159.22	C-10	115.23	154.17	21.14 ^{a)}
			O=C	167.61	167.44	—	—	O=C	168.40	168.51	168.56
				168.69	168.18	—	—		168.51	168.68	169.55

^{a)} Or vice versa.

mer **10b** to the *exo* dimer **9b** and of the *anti* isomer **11b** to the *endo* dimer **8b**. These interconversions were carried out analogously to Hammond⁷⁶⁾ who has described such thermal rearrangements for the dimers of **7a**.

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Experimental

Materials: Diene **7a** was prepared according to a literature procedure⁷⁷⁾. Dienes **7b** and **12** were prepared with reference to a study of cyclic 1,3-diacetoxy-1,3-dienes reported by Cimarusti and Wollinsky⁷⁸⁾. This method has been modified as follows: 38.4 g (0.40 mol) of 2-cyclohexenone*, 200.2 g (2.0 mol) of isopropenyl acetate and 0.2 g (1.05 mmol) of *p*-toluenesulfonic acid were refluxed for 72 h under argon. After the remaining isopropenyl acetate and acetone had been removed by distillation, the residue was distilled at reduced pressure into cooled, light-protected flasks [b.p.: 69–75°C/13 Torr, yield: 45 g (82%), **7b/12** ≈ 15/85]. As the dienes could not be separated by fractional distillation, **7b** and **12** were separated by semipreparative HPLC [ethyl acetate/*n*-hexane (3:97) as eluent]*).

7b: ¹H-NMR (90 MHz, CCl₄): δ = 2.05 (s, 3H, CH₃); 2.31 (br. s, 4H, CH₂); 5.50–5.90 (m, 3H, CH). — ¹³C-NMR (20 MHz, C₆D₆): δ = 20.57 (CH₃); 23.94, 25.82 (C-5,6); 110.98 (C-2); 123.36, 123.50 (C-3,4); 149.87 (C-1); 168.18 (C=O). — MS (70 eV): *m/z* (%) = 139 (1.2) [M⁺ +]; 138 (14.7) [M⁺]; 96 (100) [M⁺ – C₂H₂O]; 95 (56.3). — UV (CH₃CN): λ_{max} (log ε) = 262 nm (3.531).

12: ¹H-NMR (90 MHz, CCl₄): δ = 2.05 (s, 3H, CH₃); 2.22 (br. s, 4H, CH₂); 5.30 (m, 1H, 1-H); 5.70 (m, 2H, 3-H, 4-H). — ¹³C-NMR (75 MHz, C₆D₆): δ = 20.52 (CH₃); 21.59, 22.22 (C-5,6); 110.83 (C-1); 124.00, 128.63 (C-3,4); 146.51 (C-2); 168.36 (C=O). — MS (70 eV): *m/z* (%) = 139 (2.1) [M⁺ + 1]; 138 (25.5) [M⁺]; 96 (100) [M⁺ – C₂H₂O]; 95 (65.4). — UV (CH₃CN): λ_{max} (log ε) = 257 nm (3.613).

Diene **7c** was prepared by alkaline isomerization of 1-methoxy-1,4-cyclohexadiene (Janssen) under argon with sublimed potassium *tert*-butoxide in dimethyl sulfoxide analogously to literature⁸⁰⁾ (1,3-diene/1,4-diene = 80/20).

7c: ¹H-NMR (90 MHz, CCl₄): δ = 2.15 (br. s, 4H, CH₂); 3.46 (s, 3H, CH₃); 4.78 (d, *J* = 6.3 Hz, 1H, H-2); 5.30 (m, 1H, H-4); 5.70 (m, 1H, H-3). — ¹³C-NMR (75 MHz, C₆D₆): δ = 23.95, 27.35 (CH₃); 54.07 (CH₃); 92.85 (C-2); 117.86, 124.84 (C-3,4); 159.15 (C-1). — MS (70 eV): *m/z* (%) = 112 (0.5) [M⁺ + 2]; 111 (7.1) [M⁺ + 1]; 110 (100) [M⁺]; 109 (64.5); 95 (47.4) [M⁺ – CH₃]. — UV (CH₃CN): λ_{max} (log ε) = 269 nm (3.708).

Diene **18** (Janssen) was purified by distillation under argon, diene **21** was prepared according to the literature⁸¹⁾. 1,2,4-trimethoxybenzene (TMB) and 1,4-dimethoxybenzene (DMB) (both from Janssen) were purified by distillation under reduced pressure. Electron acceptors **1**⁸²⁾, **2**⁸³⁾, and **6**⁸⁴⁾ were prepared according to the cited literature procedures; **3** (Aldrich) was used without further purification.

* The 2-cyclohexenone prepared according to Tietze and Eicher⁷⁹⁾ contained about 15% of 3-cyclohexenone, which obviously caused the formation of **7b**. **7b** contained 10–12% of cyclohexenyl acetate according to GC-MS analysis, obviously caused by traces of cyclohexanone in the starting material. In the reactions with **7b**, a conversion of acetoxy-cyclohexen has not been observed.

tion, **4** (Aldrich) was recrystallized twice from petroleum ether and **5** (Fluka) from benzene and acetonitrile. LiClO₄ (Janssen) was dried at 160°C and 0.01 Torr, tetra-*n*-butylammonium tetrafluoroborate (Fluka) was recrystallized from ethyl acetate and dried at 0.001 Torr. HSbCl₆ was simply formed from SbCl₅ and gaseous HCl at –30°C in 1,1,2-trichlorotrifluoroethane as described by Gassman⁸⁵⁾.

Spectrophotometric-grade solvents (Fluka, Merck) were used for analytical purposes, for preparative procedures the solvents were purified by standard methods. In addition, acetonitrile, dichloromethane, benzene and ethyl acetate were filtered over basic alumina, which had been activated by annealing at 0.01 Torr. All procedures for purification and synthesis were carried out under argon atmosphere.

Chromatographic Equipment: Gaschromatographic analyses: Carlo Erba Fractovap 2200; Apiezon L, OV101 and OV17 glass columns, 5–10% on chromosorb WAW DMCS 80/100 mesh. — Semipreparative separations of product mixtures: either GC (F + M 720, OV101) or HPLC (Gilson-303 chromatograph, Merck Lichrosorb Si60) or column chromatography. — Analytical HPLC: Perkin Elmer Ser. 3-LC-65T model with the same column type.

Instrumental Analysis: IR spectra: Perkin-Elmer 377 and 1700 spectrometers. — ¹H-NMR spectra: Varian EM 390 (90 MHz) and VXR 300 (300 MHz). — ¹³C-NMR spectra: Varian CFT 20 (20 MHz), VXR 300 (75 MHz), and Bruker WH 270 (68 MHz) spectrometers. TMS as internal standard. — GC-MS: Varian MAT 212, 70 eV. — Absorption spectra: Perkin-Elmer 320 spectrometer. — For emission spectra (Stern-Volmer analysis) and fluorescence lifetime measurements see ref.^{86a)}. — Cyclic Voltammetry: Voltage Scan Generator (Mod. VSG 72H) and Potential Control Amplifier (Mod. PCA 72H) (both from G. Bank Elektronik).

Irradiations and Product Isolation: Irradiations for analytical purposes were performed in a “merry-go-round” apparatus (from H. Mangels, Bornheim-Roisdorf), those for preparative purposes in a photoreactor, both fitted with an immersion well (pyrex or quartz glass, water cooling) and a high-pressure mercury lamp HPK 125 W (Philips). When needed, a light filter permeable for λ ≥ 350 nm was used. In order to prevent acid-catalyzed side reactions, all glass ware was immersed in an aqueous sodium hydroxide solution for ca. 12 h. The reaction mixtures were checked by analytical GC with internal standards and worked up as follows: After removal of the solvent by distillation at room temp., the products were extracted with mixtures of ethyl acetate (3–60%) in *n*-hexane (or cyclohexane). These solutions were filtered over activated basic alumina, and the product mixtures were separated by standard methods: semipreparative HPLC, column chromatography [mixtures of ethyl acetate (3–60%) in *n*-hexane (or cyclohexane) as eluents], semipreparative GC, or distillation. Product identification of analytical irradiations was carried out by comparison with authentic samples. In addition, the reaction mixtures were stored in the dark to prove that product formation was due to photoreaction. A parallel blank reaction (control), omitting only the electron-transfer sensitizer, was irradiated in each case to establish the negligibility of direct photo-reactions bypassing the sensitizer.

Catalysis by 1 or HSbCl₆: Reactions with **1** as electron acceptor were carried out under argon at 0°C in dichloromethane as solvent. These reactions were usually complete within 5–30 minutes; product formation and conversion of the starting materials were monitored by GC analysis. After completion of the reaction, the mixtures were worked up as described previously. Reactions with HSbCl₆ as catalyst were carried out in the same way. The acid was quenched by adding triethylamine.

1. *Dimerization of 7a*: A solution of 4.0 g (0.05 mol) of **7a** and 0.158 g (0.4 mmol) of **6** in 100 ml of dichloromethane was irradiated for 16 h at $\lambda \geq 350$ nm. Work-up of the reaction mixture implied extraction of the products with 3% ethyl acetate in *n*-hexane. The isomers **8a** and **9a**, isolated together, were further purified by HPLC (6% ethyl acetate in *n*-hexane, flow 10 ml/min, retention time for **8a** and **9a**: 1.9 min).

endo- and exo-Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (8a and 9a): Colorless oil, yield 3.0 g (75%). — IR (neat): 3040, 3020 cm^{-1} (=CH); 2920, 2860 (CH); 1640 (C=O). — $^1\text{H-NMR}$: see ref.^{75). — $^{13}\text{C-NMR}$: see Table 13. — MS (70 eV): **8a**: m/z (%) = 161 (1.0) [$\text{M}^+ + 1$]; 160 (6.6) [M^+]; 80 (100) [**7a**⁺]. **9a**: m/z (%) = 161 (0.7) [$\text{M}^+ + 1$]; 160 (5.3) [M^+]; 80 (100) [**7a**⁺].}

$\text{C}_{12}\text{H}_{16}$ (160.3) Calcd. C 89.94 H 10.06
Found C 89.70 H 10.09

The dimerization of **7a** under triplet conditions was carried out according to a literature procedure^{86b}.

all-cis- and trans,cis,trans-Tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene (10a and 11a) and Dimer 9a: IR (neat): 3020 cm^{-1} (=CH); 2920, 2840 (CH); 1680, 1640 (C=C). — $^1\text{H-NMR}$: see ref.^{75). — $^{13}\text{C-NMR}$: see Tables 12 and 13. — MS (70 eV): **10a**: m/z (%) = 160 (0.4) [M^+]; 80 (100) [**7a**⁺]. **11a**: m/z (%) = 161 (0.1) [$\text{M}^+ + 1$]; 160 (0.5) [M^+]; 80 (100) [**7a**⁺].}

$\text{C}_{12}\text{H}_{16}$ (160.3) Calcd. C 89.94 H 10.06
Found C 89.70 H 10.16

2. *Dimerization of 7b*. — a) *5/LiClO₄ as Acceptor System*: A solution of 2.1 g (15 mmol) of **7b**, 0.148 g (0.6 mmol) of **5**, and 0.638 g (6 mmol) of LiClO₄ in 30 ml of acetonitrile was irradiated for 96 h at $\lambda \geq 350$ nm. After working up the reaction mixture, the products were extracted with 10% ethyl acetate in cyclohexane and separated by HPLC (Dynamax Si60, 8% ethyl acetate in cyclohexane, flow: 13.5 ml/min, retention time for **8b**: 16.8, **9b**: 15.3, **10b**: 22.7, **11b**: 18.0 min). Yield **8b**–**11b**: 0.7 g (68%).

endo-1,4-Diacetoxytricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (8b): Colorless oil. — IR (CCl₄): 3050 cm^{-1} (=CH); 2940, 2870 (CH); 1750, 1735 (C=O); 1670 (C=C). — $^1\text{H-NMR}$ (90 MHz, CCl₄): δ = 2.01 (s, 3H, CH₃); 2.04 (s, 3H, CH₃); 0.90–2.15 (m, 9H, 7-H, CH₂); 2.37 (m, 1H, 8-H); 2.92 (d/d/t, $^3J_{2,7} = 9.6/3J_{2,3} = 3.0/J = 1.8$ Hz, 1H, 2-H); 5.28 (d/t, $^3J_{2,3} = 3.0/4J_{1,3}$ Hz, 1H, 3-H); 6.05 (d/d, $^3J_{9,10} = 8.7/3J_{8,9} = 7.2$ Hz, 1H, 9-H); 6.05 (d/d, $^3J_{9,10} = 8.7$ Hz, 1H, 10-H). — $^{13}\text{C-NMR}$: see Table 13. — MS (70 eV): m/z (%) = 276 (0.2) [M^+]; 234 (0.6) [$\text{M}^+ - \text{C}_2\text{H}_2\text{O}$]; 174 (3.1); 139 (3.1) [**7b**⁺ + 1]; 138 (29.9) [**7b**⁺]; 97 (8.6); 96 (100) [**7b**⁺ - C₂H₂O].

$\text{C}_{16}\text{H}_{20}\text{O}_4$ (276.3) Calcd. C 69.55 H 7.30
Found C 69.35 H 7.47

exo-1,4-Diacetoxytricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (9b): Colorless crystals, m.p. 78°C. — IR (CCl₄): 3040 cm^{-1} (=CH); 2940, 2880 (CH); 1750, 1735 (C=O); 1680 (C=C). — $^1\text{H-NMR}$ (90 MHz, CCl₄): δ = 2.02 (s, 3H, CH₃); 2.05 (s, 3H, CH₃); 0.91–2.15 (m, 9H, 7-H, CH₂); 2.32 (m, 1H, 8-H); 2.73 (d/m, $^3J_{2,7} = 10.0$ Hz, 1H, 2-H); 5.29 (m, 1H, 3-H); 6.22 (d/d, $^3J_{9,10} = 9.0/3J_{8,9} = 6.0$ Hz, 1H, 9-H); 6.35 (d/d, $^3J_{9,10} = 9.0/4J_{1,2} = 1.2$ Hz, 1H, 10-H). — $^{13}\text{C-NMR}$: see Table 13. — MS (70 eV): m/z (%) = 276 (0.1) [M^+]; 234 (0.4) [$\text{M}^+ - \text{C}_2\text{H}_2\text{O}$]; 174 (1.8); 139 (3.1) [**7b**⁺ + 1]; 138 (31.4) [**7b**⁺]; 97 (8.2); 96 (100) [**7b**⁺ - C₂H₂O].

$\text{C}_{16}\text{H}_{20}\text{O}_4$ (276.3) Calcd. C 69.55 H 7.30
Found C 69.41 H 7.46

all-cis-4,11-Diacetoxytricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene (10b): Colorless crystals, m.p. 104°C. — IR (KBr): 3050, 3020 cm^{-1} (=CH); 2960, 2930, 2850 (CH); 1745 (C=O); 1680 (C=C). — $^1\text{H-NMR}$

(300 MHz, C₆D₆): δ = 1.67 (s, 6H, CH₃); 1.61 (d/q, $^2J_{6\text{eq},\text{ax}} = ^2J_{9\text{eq},\text{ax}} = 13.3/J = 6.5$ Hz, 2H, 6-H_{eq}, 9-H_{eq}); 1.87 (d/q, $^2J_{6\text{eq},\text{ax}} = ^2J_{9\text{eq},\text{ax}} = 13.3/J = 6.9$ Hz, 2H, 6-H_{ax}, 9-H_{ax}); 2.14 (t/m, $^3J_{5,6} = ^3J_{9,10} = 6.4$ Hz, 4H, 5-H₂, 10-H₂); 2.32 (m, $\Sigma J = 23.5$ Hz, 2H, 7-H, 8-H); 2.81 (d/m, $^3J_{2,7} = ^3J_{1,8} = 7.0$ Hz, 2H, 1-H, 2-H); 5.39 (d/t, $^3J_{2,3} = ^3J_{1,2} = 3.5/J = 1.4$ Hz, 2H, 3-H, 12-H). — $^{13}\text{C-NMR}$: see Table 12. — MS (70 eV): m/z (%) = 234 (0.1) [$\text{M}^+ - \text{C}_2\text{H}_2\text{O}$]; 139 (2.1) [**7b**⁺ + 1]; 138 (19.3) [**7b**⁺]; 97 (8.3); 96 (100) [**7b**⁺ - C₂H₂O].

$\text{C}_{16}\text{H}_{20}\text{O}_4$ (276.3) Calcd. C 69.55 H 7.30
Found C 69.23 H 7.38

trans,cis,trans-4,11-Diacetoxytricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene (11b): Colorless crystals, m.p. 82°C. — IR (CCl₄): 3050, 3020 cm^{-1} (=CH); 2920, 2840 (CH); 1750 (C=O); 1680 (C=C). — $^1\text{H-NMR}$ (300 MHz, C₆D₆): δ = 1.75 (s, 6H, CH₃); 1.45 (m, 4H, 6-H₂, 9-H₂); 2.05 (d/t, $^2J_{\text{seq},\text{ax}} = ^2J_{10\text{eq},\text{ax}} = 17.0/3J_{\text{seq},6} = ^3J_{9,10\text{eq}} = 4.2$ Hz, 2H, 5-H_{eq}, 10-H_{eq}); 2.36 (d/d/d/t, $^2J_{5\text{ax},\text{eq}} = ^2J_{10\text{ax},\text{eq}} = 17.0/3J_{5\text{ax},6} = ^3J_{9,10\text{ax}} = 9.6/7.7/J = 2.2$ Hz, 2H, 5-H_{ax}, 10-H_{ax}); 2.31 (m, $\Sigma J \leq 13.0$ Hz, 2H, 7-H, 8-H); 2.50 (m, $\Sigma J = 15.0$ Hz, 2H, 1-H, 2-H); 5.48 (d/d, $^3J_{2,3} = ^3J_{1,2} = 4.2/J = 2.2$ Hz, 2H, 3-H, 12-H). — $^{13}\text{C-NMR}$: see Table 12. — MS (70 eV): m/z (%) = 276 (0.01) [M^+]; 234 (0.2) [$\text{M}^+ - \text{C}_2\text{H}_2\text{O}$]; 139 (2.4) [**7b**⁺ + 1]; 138 (21.9) [**7b**⁺]; 97 (7.8); 96 (100) [**7b**⁺ - C₂H₂O].

$\text{C}_{16}\text{H}_{20}\text{O}_4$ (276.3) Calcd. C 69.55 H 7.30
Found C 69.54 H 7.52

b) **1 as Electron-Acceptor**: 5.53 g (0.04 mol) of **7b** and 1.63 g (2 mmol) of **1** in 100 ml of dichloromethane were stirred for 30 min at 0°C. The products were isolated as described previously. Yield **8b** and **9b**: 3.0 g (55%). The spectroscopic data of the separated isomers were identical with those of the isomers **8b** and **9b** isolated in the photochemical reaction (see above).

c) *Thermolysis of 10b and 11b*: The thermolysis experiments were carried out in sealed glass tubes at 170°C (3 h, **10b**) and 190°C (5 h, **11b**), respectively.

3. *Dimerization of 7c*: The dimerization of **7c** as electron acceptor was carried out as described by Bauld^{63,64}.

endo- and exo-1,4-Dimethoxytricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (8c and 9c): IR (neat): 3040 cm^{-1} (=CH); 2930, 2860 (CH); 2820 (OCH₃); 1660 (C=C). — $^1\text{H-NMR}$ (300 MHz, C₆D₆): **8c**: δ = 1.22–2.0 (m, 10 H, 7-H, 8-H, CH₂); 2.58 (d/m, $^3J_{2,7} = 10.0$ Hz, 1H, 2-H); 3.24 (s, 3H, 1-CH₃); 3.33 (s, 3H, 4-CH₃); 4.99 (d, $J = 2.7$ Hz, 1H, 3-H); 5.96 (d/d, $^3J_{9,10} = 8.7/3J_{8,9} = 6.3$ Hz, 1H, 9-H); 6.22 (d, $^3J_{9,10} = 8.7$ Hz, 1H, 10-H). **9c**: δ = 1.22–2.0 (m, 10 H, 7-H, 8-H, CH₂); 2.44 (d/q, $^3J_{2,7} = 11.4/J = 2.5$ Hz, 1H, 2-H); 3.26 (s, 3H, 1-CH₃); 3.34 (s, 3H, 4-CH₃); 4.86 (t, $J = 2.0$ Hz, 1H, 3-H); 6.25 (d/d, $^3J_{9,10} = 8.7/3J_{8,9} = 6.3$ Hz, 1H, 9-H); 6.40 (d/d, $^3J_{9,10} = 8.7/4J = 0.7$ Hz). — $^{13}\text{C-NMR}$: see Table 13. — MS (70 eV): **8c**: m/z (%) = 221 (0.6) [$\text{M}^+ + 1$]; 220 (3.6) [M^+]; 111 (7.9) [**7c**⁺ + 1]; 110 (100) [**7c**⁺]; 109 (8.3); 95 (9.6). **9c**: m/z (%) = 221 (0.4) [$\text{M}^+ + 1$]; 220 (2.4) [M^+]; 111 (8.2) [**7c**⁺ + 1]; 110 (100) [**7c**⁺]; 109 (8.2); 95 (9.6).

4. *Dimerization of 12*: A solution of 10.5 g (76 mmol) of **12**, 0.535 g (3 mmol) of **2**, and 3.19 g (30 mmol) of LiClO₄ in 150 ml of acetonitrile was irradiated for 90 h at $\lambda \geq 300$ nm. After working up the reaction mixture, the products were extracted with 25% ethyl acetate in cyclohexane and separated by HPLC (Dynamax Si60, 6% ethyl acetate in cyclohexane, flow: 15 ml/min, retention time for **13**: 24.9, **14**: 34.5, **15**: 40.0, **16**: 24.9, **17**: 26.7 min). Yield **13**–**17**: 4.5 g (43%).

endo-3,9-Diacetoxytricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (13): Colorless oil. — IR (CCl₄): 3060 cm^{-1} (=CH); 2940, 2860 (CH); 1755 (C=O); 1660 (C=C). — $^1\text{H-NMR}$ (300 MHz, C₆D₆): δ = 1.82 (s,

3H, CH₃); 1.83 (s, 3H, CH₃); 1.10 and 1.64 (m, m, 2H, 11-H₂); 1.48 and 1.74 (m, m, 2H, 12-H₂); 1.93 (m, 2H, 5-H₂); 1.27 and 1.38 (m, m, 2H, 6-H₂); 2.66 (m, $\Sigma J = 16$ Hz, 1H, 1-H); 2.21 (m, $\Sigma J = 32$ Hz, 1H, 7-H); 2.49 (d/m, $^3J_{2,7} = 11$ Hz, 1H, 2-H); 2.30 (quint, $J = 2.7$ Hz, 1H, 8-H); 5.75 (d/d, $^3J_{8,9} = 8.4$ Hz, $^4J = 2.2$ Hz, 1H, 10-H); 5.69 (d/d/d, $^3J_{4,5} = 5.2$ Hz, $^3J_{4,5} = 3.3$ Hz, $^4J = 3.0$ Hz, 1H, 4-H). — ¹³C-NMR: see Table 13. — MS (70 eV): m/z (%) = 277 (0.1) [M⁺ + 1]; 276 (0.7) [M⁺]; 234 (0.7) [M⁺ - C₂H₂O]; 139 (4.9) [12⁺ + 1]; 138 (23.9) [12⁺]; 97 (12.7); 96 (100) [12⁺ - C₂H₂O].

C₁₆H₂₀O₄ (276.3) Calcd. C 69.55 H 7.30
Found C 69.72 H 7.50

3,10-Diacetoxytricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (14): Colorless oil. — IR (CCl₄): 3060 cm⁻¹ (=CH); 2930, 2880 (CH); 1750 (C=O); 1660 (C=C). — ¹H-NMR (300 MHz, C₆D₆): $\delta = 1.68$ (s, 3H, CH₃); 1.73 (s, 3H, CH₃); 1.61 and 1.78 (m, m, 2H, 11-H₂); 1.09 and 1.70 (m, m, 2H, 12-H₂); 1.92 (m, 2H, 5-H₂); 1.21 and 1.34 (m, m, 2H, 6-H₂); 1.76 (m, 1H, 7-H); 2.18 (d/q, $^3J_{8,9} = 7.3$ Hz, $^3J = 2.7$ Hz, 1H, 8-H); 2.80 (m, $\Sigma J = 10.5$ Hz, 1H, 1-H); 2.90 (d/m, $^3J_{2,7} = 11$ Hz, 1H, 2-H); 5.65 (d/d/d, $^3J_{4,5} = 5.6$ Hz, $^3J_{4,5} = 3.6$ Hz, $^4J = 2.3$ Hz, 1H, 4-H); 5.89 (d/d, $^3J_{8,9} = 7.3$ Hz, $^4J = 2.2$ Hz, 1H, 9-H). — ¹³C-NMR: see Table 13. — MS (70 eV): m/z (%) = 276 (0.03) [M⁺]; 234 (0.5) [M⁺ - C₂H₂O]; 139 (1.1) [12⁺ + 1]; 138 (7.7) [12⁺]; 97 (12.9); 96 (100) [12⁺ - C₂H₂O].

C₁₆H₂₀O₄ (276.3) Calcd. C 69.55 H 7.30
Found C 69.47 H 7.42

trans,cis,trans-3,12-Diacetoxytricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene or trans,cis,trans-6,12-Diacetoxytricyclo[6.4.0.0^{2,7}]dodeca-5,11-diene (15): Colorless crystals, m.p. 77°C. — IR (CCl₄): 3020 cm⁻¹ (=CH); 2920, 2840 (CH); 1750 (C=O); 1680 (C=C). — ¹H-NMR (300 MHz, C₆D₆): $\delta = 1.83$ (s, 6H, CH₃); 1.98 (m, 4H, 5-H₂, 10-H₂); 1.23 (m, 4H, 6-H₂, 9-H₂); 2.38 (d/m, 2H, $^3J_{2,7} = ^3J_{1,8} = 5.6$ Hz, 2H, 7-H, 8-H); 2.95 (d/m, $^3J_{2,7} = ^3J_{1,8} = 5.6$ Hz, 2H, 1-H, 2-H); 5.49 (d/d, $^3J_{4,5} = ^3J_{10,11} = 5.4/3.0$ Hz, 2H, 4-H, 11-H). — ¹³C-NMR: see Table 12. — MS (70 eV): m/z (%) = 276 (0.1) [M⁺]; 234 (4.1) [M⁺ - C₂H₂O]; 139 (2.0) [12⁺ + 1]; 138 (14.3) [12⁺]; 97 (11.0); 96 (100) [12⁺ - C₂H₂O].

C₁₆H₂₀O₄ (276.3) Calcd. C 69.55 H 7.30
Found C 69.22 H 7.23

trans,cis,trans-1,2-Diacetoxytricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene or trans,cis,trans-1,7-Diacetoxytricyclo[6.4.0.0^{2,7}]dodeca-5,11-diene (16): Colorless solid, m.p. < room temp. — IR (CCl₄): 3030 cm⁻¹ (=CH); 2920, 2840 (CH); 1740 (C=O); 1440, 1430 (C=C). — ¹H-NMR (300 MHz, C₆D₆): $\delta = 1.36$ (d/d/m, $^2J_{6eq,ax} = ^2J_{9eq,ax} = 13.5/3J_{5ax/6eq} = ^3J_{9eq,10ax} = 6.5$ Hz, 2H, 6-H_{ax}, 9-H_{eq}); 1.71 (s, 6H, CH₃); 1.81 (d/d/d/t, $^2J_{5ax,eq} = ^2J_{10ax,eq} = 18.0/3J_{5ax/6ax} = ^3J_{9ax,10ax} = 11.5/3J_{5ax/6eq} = ^3J_{9eq,10ax} = 6.5$ Hz, 2H, 5-H_{ax}, 10-H_{ax}); 1.95 (d/t/t, $^2J_{5eq,ax} = ^2J_{10eq,ax} = 18.0/3J_{5eq/6ax} = ^3J_{9ax,10eq} = 6.0$ Hz, 2H, 5-H_{eq}, 10-H_{eq}); 2.12 (d/d/d/t, $^2J_{6ax,eq} = ^2J_{9ax,eq} = 13.5/3J_{5ax/6ax} = ^3J_{9ax,10ax} = 11.5/3J_{5eq,6ax} = ^3J_{9ax,10eq} = 6.0$ Hz, 2H, 6-H_{ax}, 9-H_{ax}); 2.24 (br. s. $\Sigma J = 5.0$ Hz, 2H, 7-H, 8-H); 5.96 (d/d/d, $^3J_{3,4} = ^3J_{11,12} = 10.5/3J_{4,5eq} = ^3J_{10eq,11} = 6.0$ Hz, 2H, 4-H, 11-H); 6.16 (d/m, $^3J_{3,4} = ^3J_{11,12} = 10.5$ Hz, 2H, 3-H, 12-H). — ¹³C-NMR: see Table 12. — MS (70 eV): m/z (%) = 276 (0.1) [M⁺]; 234 (0.8) [M⁺ - C₂H₂O]; 139 (5.0) [12⁺ + 1]; 138 (27.1) [12⁺]; 97 (19.5); 96 (100) [12⁺ - C₂H₂O].

C₁₆H₂₀O₄ (276.3) Calcd. C 69.55 H 7.30
Found C 69.30 H 7.47

all-cis-1,3-Diacetoxytricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene (17): Colorless oil. — IR (CCl₄): 3030 cm⁻¹ (=CH); 2920, 2840 (CH); 1750, 1730 (C=O); 1680 (C=C). — ¹H-NMR (300 MHz, C₆D₆): $\delta = 1.22$ (m, 2H, 6-H₂); 1.30 and 1.70 (m, m, 2H, 9-H₂); 1.79 (s, 3H,

CH₃); 1.80 (m, 2H, 10-H₂); 1.94 (s, 3H, CH₃); 2.00 (m, 2H, 5-H₂); 2.02 (m, 1H, 7-H); 2.51 (d/m, $^3J_{7,8} = 10.0$ Hz, 1H, 8-H); 3.41 (d/m, $^3J_{2,7} = 7.8$ Hz, 1H, 2-H); 5.63 (d/d, $^3J_{4,5} = 5.6$ Hz, $^4J = 3.0$ Hz, 1H, 4-H); 6.54 (d/m, $^3J_{11,12} = 10.5$ Hz, 1H, 12-H); 5.78 (d/m, $^3J_{11,12} = 10.5$ Hz, 1H, 11-H). — ¹³C-NMR: see Table 13. — MS (70 eV): m/z (%) = 276 (0.1) [M⁺]; 234 (2.6) [M⁺ - C₂H₂O]; 139 (5.0) [12⁺ + 1]; 138 (20.9) [12⁺]; 97 (13.9); 96 (100) [12⁺ - C₂H₂O].

C₁₆H₂₀O₄ (276.3) Calcd. C 69.55 H 7.30
Found C 69.22 H 7.23

5. Diels-Alder Reaction between 7a and 18: A solution of 1.603 g (0.02 mol) of **7a**, 11.019 g (0.1 mol) of **18**, and 2.04 g (2.5 mmol) of **1** in 100 ml of dichloromethane was stirred for 30 min at 0°C. After working up the reaction mixture, the products were extracted with 3% ethyl acetate in *n*-hexane and separated by GC.

endo- and exo-5,5-Dimethyl-6-(2'-methyl-1'-propenyl)-bicyclo[2.2.2]oct-2-ene (19 and 20). — **19**: Colorless oil, yield 1.3 g (34%). — ¹H-NMR (90 MHz, CCl₄): $\delta = 0.65$ [s, 3H, 5-CH₃ (b)]; 1.05 [s, 3H, 5-CH₃ (a)]; 1.58 (d, $^4J_{1,2} = 1.3$ Hz, 3H, 2'-CH₃); 1.63 (d, $^4J_{1,2} = 1.3$ Hz, 3H, 2'-CH₃); 0.80–1.90 (m, 4H, CH₂); 2.00 and 2.20 (m, m, 2H, 1-H, 4-H); 2.12 (d/d, $^3J_{6,1} = 10.2/3J_{6,1} = 1.8$ Hz, 1H, 6-H); 4.79 (d/sept, $^3J_{6,1} = 10.2/4J_{1,2} = 1.3$ Hz, 1H, 1'-H); 6.10 and 6.30 (m, m, 2H, 2-H, 3-H). — ¹³C-NMR (20 MHz, CCl₄/C₆D₆): $\delta = 17.80$ [2'-CH₃ (a)]; 21.23, 25.15 (C-7,8); 25.85 [2'-CH₃ (b)]; 27.32, 31.10 (5-CH₃); 37.99, 42.99, 49.73 (C-1,4,6); 39.07 (C-5); 128.89 (C-2); 129.04, 130.75, 136.56 (C-2,3,1'). — MS (70 eV): m/z (%) = 191 (0.1) [M⁺ + 1]; 190 (0.7) [M⁺]; 111 (8.6) [18⁺ + 1]; 110 (100) [18⁺]; 95 (37.0); 80 (6.8) [7a⁺].

20: Colorless oil, yield 1.0 g (26%). — ¹H-NMR (90 MHz, CCl₄): $\delta = 0.82$ [s, 3H, 5-CH₃ (b)]; 0.84 [s, 3H, 5-CH₃ (a)]; 0.70–1.05 [m, 2H, 7-H (a), 8-H (a)]; 1.58 (d, $^4J_{1,2} = 1.4$ Hz, 3H, 2'-CH₃); 1.71 (d, $^4J_{1,2} = 1.4$ Hz, 3H, 2'-CH₃); 1.60–1.95 [m, 2H, 7-H (b), 8-H (b)]; 1.92 (d/d, $^3J_{6,1} = 10.2/3J_{6,1} = 3.0$ Hz, 1H, 6-H); 1.98 and 2.08 (m, m, 2H, 1-H, 4-H); 5.28 (d/sept, $^3J_{6,1} = 10.2/4J_{1,2} = 1.4$ Hz, 1H, 1'-H); 6.21 (m, 2H, 2-H, 3-H). — ¹³C-NMR (20 MHz, CCl₄/C₆D₆): $\delta = 17.96$ [2'-CH₃ (a)]; 16.88, 21.94 (C-7,8); 25.40 [2'-CH₃ (b)]; 26.32, 33.37 (5-CH₃); 34.97 (C-5); 37.12, 42.67, 45.25 (C-1,4,6); 130.76 (C-2); 125.10, 133.51, 134.60 (C-2,3,1'). — MS (70 eV): m/z (%) = 191 (0.1) [M⁺ + 1]; 190 (0.3) [M⁺]; 111 (9.0) [18⁺ + 1]; 110 (100) [18⁺]; 95 (43.4); 80 (7.1) [7a⁺].

6. Diels-Alder Reaction between 7a and 21: A solution of 4.01 g (0.05 mol) of **7a**, 8.61 (0.1 mol) of **21**, and 8.16 (0.01 mol) of **1** in 100 ml of dichloromethane was stirred for 20 min at 0°C. After working up to reaction mixture, the products were extracted with 15% ethyl acetate in *n*-hexane and separated by HPLC (Si60, 18% ethyl acetate in *n*-hexane, flow: 15 ml/min, retention time of **8a** and **9a**: 7.0, **22a**: 29.0, **23a**: 13.4 min).

endo-3,6-Dioxatricyclo[6.4.0.0^{2,7}]dodec-9-ene (22a): Colorless solid, m.p. 35°C, yield 1.0 g (12%). — IR (KBr): 3050 cm⁻¹ (=CH); 2950, 2860 (CH); 1630 (C=C). — ¹H-NMR (90 MHz, CCl₄): $\delta = 1.18$ –1.48 (m, 4H, 11-H₂, 12-H₂); 2.62 (m, 2H, 1-H, 8-H); 3.45 (t, $J = 1.3$ Hz, 2H, 2-H, 7-H); 3.32–3.73 (m, 4H, 4-H₂, 5-H₂); 6.10 (d/d, $J = 4.4/2.9$ Hz, 2H, 9-H, 10-H). — ¹³C-NMR (68 MHz, CCl₄/C₆D₆): $\delta = 21.63$ (C-11, 12); 35.39 (C-1,8); 61.51 (C-4,5); 76.01 (C-2,7); 131.38 (C-9, 10). — MS (70 eV): m/z (%) = 167 (0.3) [M⁺ + 1]; 166 (2.4) [M⁺]; 87 (4.3) [21⁺ + 1]; 86 (100) [21⁺]; 80 (18.1) [7a⁺].

C₁₀H₁₄O₂ (166.2) Calcd. C 72.26 H 8.49
Found C 72.14 H 8.58

exo-3,6-Dioxatricyclo[6.4.0.0^{2,7}]dodec-9-ene (23a): Colorless oil, yield 0.5 g (6%). — IR (neat): 3040 cm⁻¹ (=CH); 2960, 2940, 2860 (CH); 1630 (C=C). — ¹H-NMR (90 MHz, CCl₄): $\delta = 0.95$ [d/m, $J = 7$ Hz, 2H, 11-H (a), 12-H (a)]; 2.00 [d/m, $J = 7$ Hz, 2H,

11-H (b), 12-H (b)]; 2.58 (m, 2H, 1-H, 8-H); 3.03 (t, $J = 1.8$ Hz, 2H, 2-H, 7-H); 3.32 [m, 2H, 4-H (b), 5-H (b)]; 3.81 [m, 2H, 4-H (a), 5-H (a)]; 6.12 (d/d, $J = 4.8/3.1$ Hz, 2H, 9-H, 10-H). — $^{13}\text{C-NMR}$ (68 MHz, $\text{CCl}_4/\text{C}_6\text{D}_6$): $\delta = 18.04$ (C-11,12); 34.97 (C-1,8); 61.35 (C-4,5); 70.19 (C-2,7); 133.13 (C-9,10). — MS (70 eV) m/z (%) = 167 (0.2) [$\text{M}^+ + 1$]; 166 (1.4) [M^+]; 87 (4.9) [$21^+ + 1$]; 86 (100) [21^+]; 80 (17.5) [$7a^+$].

$\text{C}_{10}\text{H}_{14}\text{O}_2$ (166.2) Calcd. C 72.26 H 8.49
Found C 72.99 H 8.63

7. Diels-Alder Reaction between 12 and 21: A solution of 2.76 g (0.02 mol) of **12**, 8.6 g (0.1 mol) of **21**, and 0.82 g (1 mmol) of **1** in 100 ml of dichloromethane was stirred for 30 min at 0°C. After working up the reaction mixture, the products were extracted with 60% ethyl acetate in *n*-hexane and separated by column chromatography (60% ethyl acetate in *n*-hexane as eluant, **22b**: $R_f = 0.68$, **23b**: $R_f = 0.54$).

endo-10-Acetoxy-3,6-dioxatricyclo[6.4.0.0^{2,7}]dodeca-9-ene (22b): Colorless oil, yield 0.7 g (16%). — $^1\text{H-NMR}$ (90 MHz, CCl_4): $\delta = 1.32$ (m, 4H, 11-H₂, 12-H₂); 2.08 (s, 3H, CH₃); 2.50 (m, 1H, 8-H); 2.68 (m, 1H, 1-H); 3.44 (m, 2H, 2-H, 7-H); 3.55 (m, 4H, 4-H₂, 5-H₂); 5.56 (d/d, $J = 7.1/2.2$ Hz, 1H, 9-H). — $^{13}\text{C-NMR}$ (20 MHz, $\text{CCl}_4/\text{C}_6\text{D}_6$): $\delta = 20.40$ (CH₃); 21.34, 22.76 (C-11, 12); 35.97, 40.42 (C-1,8); 61.54, 61.64 (C-4,5); 75.89, 76.22 (C-2,7); 112.51 (C-9); 151.33 (C-10); 168.72 (C=O). — MS (70 eV): m/z (%) = 226 (0.1) [$\text{M}^+ + 2$]; 225 (0.6) [$\text{M}^+ + 1$]; 224 (3.9) [M^+]; 182 (1.0) [$\text{M}^+ - \text{C}_2\text{H}_2\text{O}$]; 139 (2.8) [$12^+ + 1$]; 138 (29.8) [12^+]; 96 (100) [$12^+ - \text{C}_2\text{H}_2\text{O}$] 86 (30) [21^+].

exo-10-Acetoxy-3,6-dioxatricyclo[6.4.0.0^{2,7}]dodeca-9-ene (23b): Colorless oil, yield 0.4 g (9%). — $^1\text{H-NMR}$ (90 MHz, CCl_4): $\delta = 1.20$ [m, 2H, 11-H (a), 12-H (a)]; 1.95 [m, 2H, 11-H (b), 12-H (b)]; 2.03 (s, 3H, CH₃); 2.50 (m, 1H, 8-H); 2.65 (m, 1H, 1-H); 3.14 (m, 2H, 2-H, 7-H); 3.38 [m, 2H, 4-H (b), 5-H (b)]; 3.78 [m, 2H, 4-H (a), 5-H (a)]; 5.55 (d/d, $J = 7.5/2.1$ Hz, 1H, 9-H). — $^{13}\text{C-NMR}$ (20 MHz, $\text{CCl}_4/\text{C}_6\text{D}_6$): $\delta = 20.89$ (CH₃); 18.38, 18.75 (C-11,12); 34.88, 39.26 (C-1,8); 61.01, 61.33 (C-4,5); 69.29, 70.88 (C-2,7); 114.01 (C-9); 152.46 (C-10); 167.88 (C=O). — MS (70 eV): m/z (%) = 225 (0.3) [$\text{M}^+ + 1$]; 224 (2.1) [M^+]; 182 (1.9) [$\text{M}^+ - \text{C}_2\text{H}_2\text{O}$]; 139 (3.3) [$12^+ + 1$]; 138 (32.2) [12^+]; 96 (100) [$12^+ - \text{C}_2\text{H}_2\text{O}$] 86 (32.2) [21^+].

Luminescence Quenching: The luminescence spectra were recorded at 20°C. Samples containing 1,4-dicyanonaphthalene (**2**) and the quencher were deoxygenated by bubbling argon through the solutions in triangular cuvettes⁸⁷. The Stern-Volmer relationship was measured over a concentration range with a factor of at least 10. No deviations other than statistical ones were observed.

Measuring of Quantum Yields, Electrochemical Redox Potentials: Values of product-quantum yields Φ_p were determined with an irradiation set-up and the potassium ferrioxalate actinometer, which has already been described elsewhere⁸⁸. The product formation, as well as the conversion of the starting material, were measured by GC (internal standard method) at max. 10% conversion. Half-peak-redox potentials were obtained by cyclic voltammetry with a platinum electrode and an Ag/0.1 M AgNO₃ reference electrode (concentration 10⁻³ M). Tetra-*n*-butylammonium tetrafluoroborate (0.1 M) was used as supporting electrolyte in acetonitrile. The scan speed was 100 mV/s; half-peak potentials were taken as the half-wave potentials. Redox potentials measured versus SCE, taken from literature⁶⁵, were fitted accordingly: $E_{1/2}(\text{Ag}/\text{Ag}^+) = E_{1/2}(\text{SCE}) - 0.3 \text{ V}$ ⁸⁹.

Note added in proof (May 19, 1988): A most recent kinetic analysis of Ebersson and Olofsson⁹⁰ of the radical-cation-catalyzed

Diels-Alder dimerization of 1,3-cyclohexadiene in the presence of tris(4-bromophenyl)ammonium hexachloroantimonate revealed that this dimerization is presumably not a radical-chain reaction. This was also indicated by the fact that tris(4-bromophenyl)amine must be present in an appreciable concentration during the reaction⁹⁰. According to a theoretical study performed by Schwarz and coworkers⁹¹ the reaction of ketone radical cation with ethylene should not be classified as a cycloaddition but rather as a nucleophilic addition. In view of the results reported here — especially because of the fact that many radical-cation Diels-Alder reactions proceed stepwise — one may also use this classification.

CAS Registry Numbers

7a: 592-57-4 / **7b:** 74502-18-4 / **7c:** 2161-90-2 / **8a:** 703-35-5 / **8b:** 96244-46-1 / **8c:** 86391-05-1 / **9a:** 703-36-6 / **9b:** 96194-84-2 / **9c:** 86336-24-5 / **10a:** 704-53-0 / **10b:** 115018-85-4 / **11a:** 670-79-1 / **11b:** 115018-86-5 / **12:** 93914-93-3 / **13:** 115018-87-6 / **14:** 115018-88-7 / **15:** 115018-92-3 / **16:** 115018-90-1 / **17:** 115018-93-4 / **18:** 764-13-6 / **19:** 76960-42-4 / **20:** 76986-20-4 / **21:** 543-75-9 / **22a:** 114288-23-2 / **22b:** 115018-94-5 / **23a:** 115074-99-2 / **23b:** 115075-00-8 / 2-cyclohexenone: 930-68-7 / isopropenyl acetate: 108-22-5 / 3-cyclohexenone: 4096-34-8 / 1-methoxy-1,4-cyclohexadiene: 2886-59-1

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