A New Type of Electron Acceptor for Diels–Alder Reactions *via* Radical Cations

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Ketone–$LiClO_4$ mixtures have been shown to be effective electron acceptors for catalysing Diels–Alder reactions, which may proceed both *via* the radical cation of the diene and *via* the radical cation of the dienophile.

Recently we have shown that ketone–$LiClO_4$ mixtures provide efficient electron acceptors for generating radical cations from alkenes upon photolysis.[1,2] Both polar solvents and the special salt effect of $LiClO_4$ increase the yield and the lifetime of the radical ions[1,2] [equation (1)].[1,2]

We now show that this type of electron acceptor catalyses cycloadditions, and compare their efficiencies with those of other known electron acceptors such as tris(*p*-bromophenyl)aminium hexachlorostibanate[3] (**4**), 2,4,6-triphenylpyrylium tetrafluoroborate[4] (**5**), and 1,4-dicyanonaphthalene[5] (**6**).

The results of the Diels–Alder dimerization of cyclohexa-

Table 1. Results from the Diels–Alder dimerization of cyclohexa-1,3-diene (**7**).

Entry	Electron acceptor[a]	Method[c]	Yield (%)	Product ratio			Ref.
				(**8**) : (**9**)	(**10**)	(**11**)	
1	(**1**)–$LiClO_4$	*h*ν	60	1 : 1	—	—	This work
2	(**2**)–$LiClO_4$	*h*ν	60	1 : 1	—	—	This work
3	(**4**)	Δ	77	4 : 1	—	—	6
4	(**5**)	*h*ν	70	6 : 1	Traces		This work, 7
5	(**6**)	*h*ν	80	4 : 1	Traces		5
6	(**6**)[b]	*h*ν	75	(1 : 6)[e]	Main products		5
7	—	Δ[d]	32	4 : 1	—	—	8, 9

[a] Max. 10 mol% in acetonitrile; (**7**), 0.5 M. [b] In benzene. [c] *h*ν, λ > 350 mm; Δ, 20 °C. [d] Thermal Diels–Alder, 200 °C, 24 h. [e] Minor products.

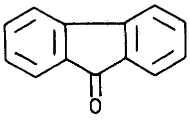
Table 2. *endo* : *exo* Ratios in the radical cation Diels–Alder reaction of (7) and (12).

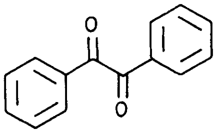
Entry	Electron acceptor[a]	Method[b]	(7) : (12)	(13) : (14)[c]
1	(4)	Δ	1 : 10	2.0 : 1
2	(4)	Δ	1 : 1	1.7 : 1
3	(4)	Δ	10 : 1	1.3 : 1
4	(1)-LiClO$_4$	$h\nu$	1 : 2	1.5 : 1
5	(1)-LiClO$_4$	$h\nu$	1 : 1	1.3 : 1
6	(3)-LiClO$_4$	$h\nu$	1 : 5	1.6 : 1
7	(5)	$h\nu$	1 : 1	1.3 : 1
8	(6)	$h\nu$	1 : 2	2.0 : 1

[a] See note a of Table 1. [b] See note c of Table 1. [c] Max. error 4% based on several measurements.

$$R_2CO + D \xrightarrow{h\nu} (R_2CO^{\delta-}D^{\delta+}) \xrightarrow{Li^+} (R_2CO^{\bullet-}Li^+) + D^{\bullet+} \quad (1)$$

R_2CO = (1), (2), or (3)   D = electron donor (*e.g.* alkene)


(1)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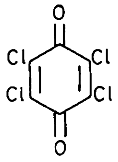
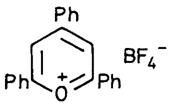

(3)

$(p\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$

(4)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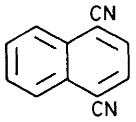
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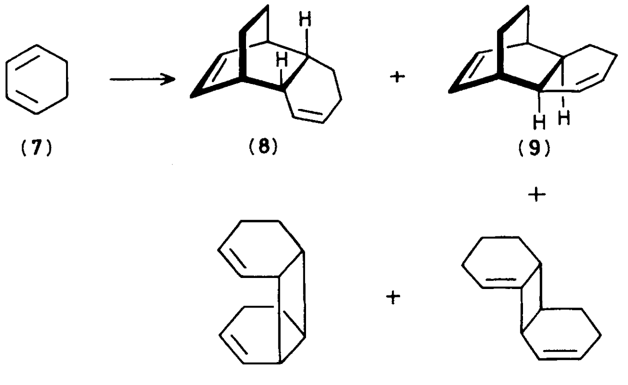
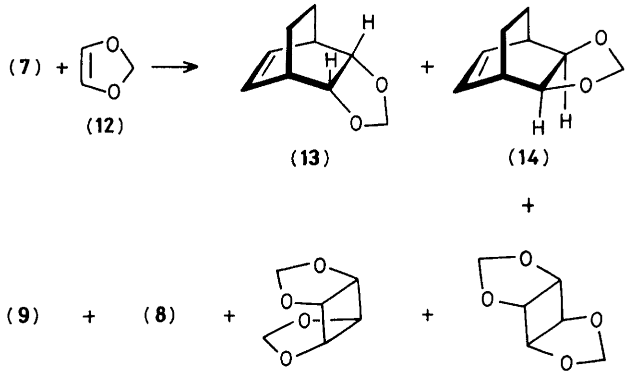

(7) (8) (9) (10) (11)


(12) (13) (14) (16) (15)

1,3-diene (7) are presented in Table 1.† They clearly show that the ketone–LiClO$_4$ system is as efficient in catalysing the formation of (8) and (9) as the other acceptors (4)—(6). Compared to the 'normal' *endo* : *exo* ratios [(8) : (9) 4 : 1] the ketone acceptors do not show any preference for one stereoisomer. This may indicate the additional involvement of a triplet reaction channel as shown by Schuster[5] (see entry 6 of Table 1) and others.[8,9]

However, the selectivity increases with the pyrylium salt (5) as catalyst (entry 4). These results indicate that all cation-radical Diels–Alder reactions cannot be simply rationalized by assuming a chain reaction.[3,6] Different types of radical ion pairs may be involved[1,2] as well as additional intermediates such as ternary complexes.[5]

Other important aspects concerning the mechanism are revealed by investigation of the mixed cycloaddition between 1,3-dioxole (12) and (7).† Here the dimerization of (12) with formation of (15) and (16) is a minor process‡ but (8) and (9) are mainly formed if an excess of (7) is used. The results in Table 2 clearly show that the *endo* : *exo* ratios depend on the ratio of the starting materials for all types of electron acceptors. The lower limit (1.3 : 1) for the various acceptors is reached for a different (7) : (12) ratio, which indicates different mechanisms.

However, there is one common feature in all cases: an excess of (12) predominantly leads to the *endo*-adduct (13). This suggests that radical cations of (12) are intermediates. With an excess of (7), however, formation of the *exo*-isomer (14) increases. Owing to the excess of cyclohexadiene and the unusually long lifetime of (7)$^{\bullet+}$ [$\tau_{1/2}$ 7.7 μs in the (3)–(7) system compared to <1 μs in other (3)–alkene systems[11]] the radical cation of the diene will be the reactive intermediate with excess of (7). This contrasts with results of Bauld[12] who has stressed the 'role selectivity' of radical cation Diels–Alder reactions, *i.e.*, only radical cations of the dienophile should yield Diels–Alder adducts.

As a consequence the scope of this type of catalysed reaction need not be limited by Bauld's principle. A reaction channel *via* the diene-radical cations should proceed in multi-step manner analogous to results of Gross[13] and Roth.[14]

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† All products have been identified either by comparison with an authentic sample or on the basis of a complete analysis of n.m.r. and mass spectral data. Protic or Lewis acids, respectively, do not catalyse the formation of the Diels–Alder adducts (see ref. 15).

‡ The dimerization of (12) using (4) as catalyst yields (15) and (16) in 1 : 1.5 ratio. This ratio is different from that which is observed for triplet-sensitization [(15) : (16) 1 : 0.6, ref. 10].

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