

Electron Transfer Reactions in Organic Chemistry. XXI.[†] New Catalysts for the Diels–Alder Dimerization of 1,3-Cyclohexadiene: Brönsted, Lewis and Redox Catalysts

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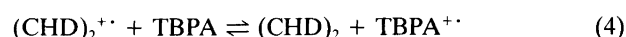
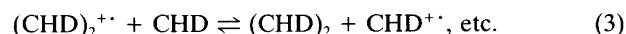
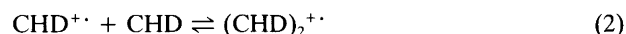
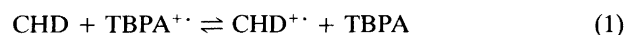
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The dimerization of a model compound, 1,3-cyclohexadiene (CHD), to give the Diels–Alder dimer [(CHD)₂] has been studied with the aim of finding other catalysts than the commonly used tris(4-bromophenyl)aminium ion (TBPA⁺). Other radical cations with redox potentials (ArH⁺/ArH) ≥ ca. 1.0 V vs. SCE worked equally well. Among inorganic species, iron(III) chloride was a good catalyst and iron(III)(phenanthroline) a slightly less efficient one. In contrast, the strong oxidants, hexachloroosmate(V), tungsten hexachloride and hexanitratocerate(IV) did not sustain DA dimerization but instead produced benzene in low yield. With trifluoroacetic acid as a catalyst, a maximum yield of 15% of the DA dimer was obtained. There was evidence for formation of a coupling product between tris(4-methoxyphenyl)aminium ion and CHD.

In the TBPA⁺-catalyzed reaction, added 'inert' anions, like perchlorate and trifluoromethanesulfonate, almost eliminated DA dimerization. These solutions displayed spectacular color changes; the original blue color of TBPA⁺ decayed very fast (seconds) and was later replaced by a new blue color (minutes) which then slowly faded away (hours). A persistent radical species (triplet, showing hyperfine coupling to one nitrogen) was detected in the solutions after the TBPA⁺-catalyzed reactions.

The finding that Diels–Alder (DA) reactions are strongly catalyzed by radical cation salts, like the commonly used electron transfer (ET) oxidant tris(4-bromophenyl)aminium ion (TBPA⁺), has greatly widened the scope of this synthetically important reaction.¹ From studies of a model system, dimerization of 1,3-cyclohexadiene (CHD), the catalytic mechanism has been suggested to be of the radical cation chain type [eqn. (1)–(3)],² although one might envisage a more conventional mechanism, if the CHD molecule of eqn. (3) is replaced by a molecule of TBPA, the most easily oxidizable component of the system, cf. eqn. (4).^{3,4}



We have performed mechanistic studies on the DA dimerization of CHD by TBPA⁺, with emphasis on the ultimate fate of the radical cation under these conditions. It

was concluded that the conventional catalytic mechanism is valid and shown that the radical cation is consumed in an oxidative addition process, formation of 1,2- and 1,4-dichloro adducts of CHD. Similar side-reactions have been detected in a recent⁵ study of the dehydrogenation of 1,4-dihydronaphthalene by TBPA⁺.

In view of the well demonstrated capacity of TBPA⁺ to act as an electrophile,^{6–8} we felt the need to explore other catalysts and catalyst types in DA dimerization for comparative purposes. In what follows, we report explorative studies of other radical cation catalysts, as well as catalysts of different reactivity type (Brönsted, Lewis acids). Iron(III) chloride, with its blend of ET and Lewis acid reactivity, turned out to be equally as effective as TBPA⁺.

Results

Brönsted acids as catalysts. Although it has been claimed that CHD dimerization is not subject to catalysis even by strong Brönsted acids,⁹ we obtained DA dimers in 10–15% yield by treating CHD with trifluoroacetic (TFA) in dichloromethane. Attempts to improve the yield by changing the reaction conditions were unsuccessful (Table 1). In runs where the yield of recovered CHD was measured, it was found to vary from 100 to 0% when the [TFA]/[CHD] ratio was changed from 0.1 to 65. A comparable dependence of

[†] Part XX, see Ref. 4.

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Table 1. GLC-detectable products from the reaction between CHD and TFA in dichloromethane at 0°C unless otherwise stated.

Reaction conditions			Yield (%) ^a of			Color changes
Time/min	[CHD]/M	[TFA]/M	Recovered CHD ^b	DA dimers (<i>endo/exo</i>)	Acyclic dimers ^c	begin → end
15	0.19	13 (neat)		0.4	5	Yellow ^d → red-brown
15	0.19	2.6		15 (3.7)	4	Yellow → orange
15	0.19	2.6 ^e		13 (3.5)	3	Yellow → red-brown
30	0.19	0.38		4 (3.3)		Colorless → light brown
30'	0.19	0.95		13 (3.7)	10	Light yellow → red-brown
15	0.19	2.6 (in CH ₃ CN)				Colorless → white turbid
30'	0.19	2.6 (in CCl ₄)		2 (7.0)	10	Colorless → light brown
15	0.10	0.01	100			Colorless
15	0.10	1.0	71.5	11 (4.9) ^g	2	Colorless → yellow
15	0.10	3.2	2.7	11 (4.0) ^h	12	Yellow → orange
15	0.10	6.5	0	5 (4.3) ^h	12	Yellow turbid → red-brown

^aBased on CHD. ^bNot determined, if not given. ^cFour isomers; trimers and tetramers were also detectable. ^dA white precipitate was formed upon mixing. ^eWith 0.002 M NOBF₄ added. ^fAt 20°C. ^gCa. 10% yield of the addition product between CHD and TFA was obtained. ^hCa. 20% yield of the addition product between CHD and TFA was obtained.

substrate recovery, as well as similar color changes, was found when styrene was treated with perchloric acid in dichloromethane.¹⁰ According to mass spectral (MS) analysis, the other dimers formed were of acyclic type in which

CHD had ring-opened.¹³ Both cyclic and acyclic dimers were formed in the TFA-catalyzed reaction of 1,1'-bicyclopentene,¹² the optimum level of [TFA] being 4%.

Table 2. GLC-detectable products from the reaction of CHD with Lewis acid catalysts in dichloromethane. Reaction period 15 min unless otherwise stated.

Reaction conditions				Yield (%) of				
Lewis acid	Mol % ^a	Temp./°C	[CHD]/mM	Recovered CHD	DA dimers ^a (<i>endo/exo</i>)	Benzene ^b	Addition products ^a	
							Dimers + HCl	Dimers + Cl ₂
FeCl ₃ · 2.5 H ₂ O	5	20	190		27 (3.6)			
	5 ^c	20	190		28 (4.0)			
	10	20	190		21 (5.0)			
	5 ^d	20	190		25 (3.3)			
	50	20	16.8	0	24 (17)	1	5	13
	50 ^e	20	16.8	100				
	50	0	16.8	0	70 (10)	1		11
	50	-50	16.8	100				
FeCl ₃ · 6 H ₂ O	50	20	16.8	51	38 (7.8)	0.5		2
	10	20	84	55	28 (4.9)	2.5		1
	50	0	16.8	88	8 (5.7)			
FeCl ₃	50	20	16.8	0	11 (4.5)	1	3	12
	50	0	16.8	0	51 (13)	1		11
	50 ^f	0	16.8	94	2 (8.1)	1		Trace
	10	0	84	24	56 (5.4)	7		3
	20	0	84	5	66 (6.2)	5	Trace	5
	10	-20	84	78	12 (4.6)	4.5	Trace	5
	50	-20	16.8	19	62 (6.6)	0.5		5
AlCl ₃	50	0	16.8	3	4 (5.2)	6.5		
TiCl ₄	50	0	16.8	8.5	1.3	4	12 ^g	
SnCl ₄	50	20	16.8	82	4 (6.3)	1		

^aBased upon CHD. ^bBased upon Lewis acid and calculated for a two-electron process; yield rounded off to the nearest 0.5.

^cReaction period 1 h. ^dReaction performed with ultrasound. ^eBu₄NPF₆ (0.01 M) added. ^f2,6-Di-(*tert*-butyl)pyridine (1.2 equiv.) added.

^gYield of the addition product of CHD and HCl, 2%.

Table 3. Products from the DA dimerization of CHD, using tris(phenanthroline)iron(III) hexafluorophosphate (ferriin) as a catalyst in dichloromethane.

Reaction conditions				Yield (%) ^a of	
Temp./°C	Reaction period/h	Ferriin (mol %)	[CHD]/mM	Recovered ^b CHD	DA dimers (<i>endo/exo</i>)
0	0.25	10	190		37 (3.8)
20	0.25	5	190		34 (3.7)
20	0.25 ^c	5	190		38 (3.8)
20	1	5	190		47 (3.9)
20	7.5	5	190		42 (3.7)
20	24	5	190		36 (3.6)
20	0.25	2	190		26 (3.8)
20	0.25	2.2	400		31 (3.8)
20	0.25	0.5	400		8 (3.4)
20	0.25	1	200		8 (3.5)
40	0.25	5	190		30 (3.5)
20	0.25	5	16.8	52	51 (6.0)
20	0.25	50	16.8	17	84 (6.5)

^aBased on CHD. ^bNot determined if not given. ^cThe ferriin mixture was stirred for 0.25 h before CHD was added.

Other protic acids were tested but with negative results. Trichloroacetic acid, known¹¹ to catalyze the dimerization of cyclopentadiene, 4-toluenesulfonic acid or an acidic ion-exchange resin (Amberlite^R CG-4B) failed to give any significant yield of DA dimers. The solutions remained colorless and with trichloroacetic acid a 5% yield of the (HCl + CHD) addition product and ca. 1% of DA dimers were obtained. Trifluoromethanesulfonic acid (10 mol %, 0°C, 15 min) immediately produced a dark red-brown solution, changing to purple, in which only traces of DA dimers were detectable (30% recovered CHD).

Thus with protic acids it was not possible to find the correct balance between too low and too high reactivity, the latter case leading to 'large amounts of intractable material'.¹⁴ A five- to ten-fold excess of TFA seems to be adequate for producing DA dimers at the 15% yield level, but strong competition from other reactions cannot be eliminated.*

Lewis acids as catalysts. Our original expectations of finding good catalysts among Lewis acids were not great, since polymerization was the expected mode of reaction.¹⁶ However, our first trial using iron(III) chloride hydrate (FeCl₃·2.5 H₂O) in a 'concentration' equal to the levels used in the TBPA⁺-catalyzed reaction¹⁷ surprisingly gave DA dimers in 27% yield (*endo/exo* ≈ 4), and the yield could subsequently be raised to 70% by increasing the amount of catalyst and decreasing [CHD] (see Table 2). This reaction proceeded under heterogeneous conditions. With anhydrous iron(III) chloride in dichloromethane the reaction could be performed in homogeneous medium [maximally 8.4 mM in Fe(III)]; the yield of DA dimer was again at best ≈ 70% with an *endo/exo* ratio of ≈ 6. The

* The possibility cannot be excluded that the catalytic activity of TFA depends on its power to oxidize organic compounds to the corresponding radical cations in a photochemical process.¹⁵ This will be examined in a future study.

reactivity of iron(III) chloride could be attenuated by using the hexahydrate, FeCl₃·6H₂O, which decreased the yield of DA dimers to ca. 40%.

In spite of the fact that it is difficult to analyze for benzene against the background level of benzene in CHD (1.5 mol %),⁴ the benzene yields reported in Table 2 do correspond to significantly larger GLC peak areas than those corresponding to background. The addition products from the dimers have acyclic structures (GLC/MS analysis).

The purpose of adding 0.01 M Bu₄NPF₆ to the reaction mixture was to increase the solubility of the ferric salt. This did not occur, but the result was nevertheless dramatic; complete suppression of DA dimerization. The reaction was also blocked by the addition of 2,6-di(*tert*-butyl)pyridine (1.2 equiv.). A similar effect is known from the TBPA⁺ catalyzed reaction,⁴ but here the blocking of DA dimerization is partially compensated by the formation of benzene (30%).

With Lewis acids of less pronounced redox reactivity than FeCl₃ (see below), such as TiCl₄ and SnCl₄, very low yields of DA dimers were obtained. The stronger oxidant, AlCl₃, did not catalyze DA dimerization but instead induced polymerization.

Inorganic ET reagents as catalysts. An Fe(III) salt with known one-electron oxidizing properties, tetrabutylammonium hexacyanoferrate(III),¹⁸ is soluble in dichloromethane and was tried as a catalyst for the DA dimerization of CHD. No reaction occurred at 20°C (1 h) and all starting material was recovered. Another well-known Fe(III) oxidant, tris(phenanthroline)iron(III), [Fe(phen)₃³⁺] with *E*^o[Fe(III)/(II)] = 0.98 V vs. SCE in acetonitrile/tetraethylammonium perchlorate (0.1 M), is considered to be a typical outer-sphere oxidant of organic compounds.¹⁹⁻²⁴ In the form of the hexafluorophosphate, Fe(phen)₃³⁺ is very sparingly soluble in dichloromethane

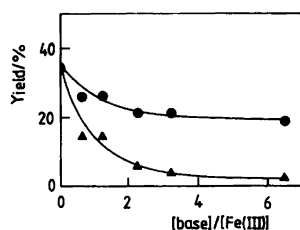


Fig. 1. Yield of DA dimers as a function of the $[\text{base}]/[\text{Fe(III)}(\text{phen})_3^{3+}]$ under heterogeneous conditions in dichloromethane at 20°C. $[\text{CHD}]_0 = 190 \text{ mM}$; $[\text{Fe(III)}] = 9.5 \text{ mM}$. ●, base = 2,6-di(*tert*-butyl)pyridine; ▲, base = 2,6-lutidine.

($\leq 0.35 \text{ mM}$). Since this solvent is probably essential for these catalyzed DA dimerizations, we used the salt under heterogeneous conditions and were able to secure high yields of DA dimers, $> 80\%$, under appropriate conditions (low $[\text{CHD}]$, high proportion of catalyst). Table 3 shows these results. No other products were obtained. It should be kept in mind that the reaction conditions were heterogeneous, as in the case of the iron(III) chloride hydrates, so that the possibility of surface reactions must be considered. Control experiments with the corresponding $\text{Fe(II)}(\text{phen})_3^{2+}$ salt produced no DA dimers. With the addition of increasing concentrations of hindered bases, such as 2,6-di(*tert*-butyl)pyridine or 2,6-lutidine, the yield was progressively lowered to ≈ 20 and 3% , respectively (Fig. 1).

Other oxidants of well-established outer-sphere oxidizing behavior toward organic compounds are 12-tungstocobaltate(III) ($\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}$),^{25,26} tungsten hexachloride,²⁷

hexachloroosmate(V),²⁸ and hexanitratocerate(IV)²⁹ (as the tetrabutylammonium salt). Except for 12-tungstocobalt(III)ate ion,²⁶ these are oxidants of redox potentials in the same range as that of TBPA^{+} , 1.06 V vs. SCE. Table 4 summarizes results from experiments with these systems, showing that none of them produced more than very low yields of DA dimers. The metal salts did undergo one-electron reduction (as evidenced by the typical associated color changes) but evidently their oxidizing power was consumed in other processes, such as oxidative polymerization. As an example, $(\text{Bu}_4\text{N}^+)_2\text{Ce}(\text{NO}_3)_6^{2-}$ was reduced completely within 10 min (yellow \rightarrow colorless), and benzene (25% yield) was formed as the only volatile product. Attempts to increase the benzene yield failed, perhaps reflecting the basicity of hexanitratocerate(IV) which is similar to that of 2,6-di(*tert*-butyl)pyridine (giving benzene in $\approx 30\%$ yield; the stronger base, 2,6-lutidine gave 43% benzene⁴).

Following an observation⁹ that zeolites are weakly active as catalysts for DA dimerization (up to 13% yield), we conducted a few experiments with the Cu(II)-containing zeolite Y, denoted $\text{Cu}^{\text{II}}\text{Y}$. The blue-green zeolite changed color directly to gray upon addition to a solution of CHD in dichloromethane. With $[\text{Cu}^{\text{II}}]/[\text{CHD}] \approx 0.9$ in this solvent, very low yields of a large number of products were obtained but in pentane a much cleaner product pattern could be obtained. The yields of GLC-detectable products were still low, benzene (5%) and DA dimers (2%) with 46% recovered CHD. Under these conditions (15 min at 20°C) no reaction occurred with either of the $\text{Na}^{\text{II}}\text{A}$ zeo-

Table 4. GLC-detectable products from the reaction between CHD and ET reagents in dichloromethane. Reaction period 15 min unless otherwise stated.

Reaction conditions				Yield (%) ^a of			Color change
ET reagent	Mol % ^b	Temp./°C	[CHD]/mM	Recovered CHD	DA dimers ^b (endo/exo)	Benzene ^c	begin \rightarrow end
Co(III)W	5 ^d	40 ^e	190		N.o.		Yellow \rightarrow green
	5 ^d	40 ^f	190		N.o.		
	5	20;40 ^g	16.8	97	N.o.	N.o.	
WCl ₆	5	20	190		4.5 (2.8) ^h		Light brown \rightarrow dark brown
	10	0	190		5.9 (2.8) ^h		
	5	20	16.8	68	16 (3.9) ^h	10	Yellow turbid \rightarrow blue-green
	50	20	16.8	0			Light brown \rightarrow dark brown
OsCl ₆ ⁻	5	20	16.8	100	N.o.	N.o.	Red-brown \rightarrow yellow ⁱ
	50	20	16.8	72	2 ^j	11	Red-brown \rightarrow green ⁱ
Ce(NO ₃) ₆ ²⁻	10	20	95	90	Trace	25	Yellow \rightarrow colorless
	10 ^k	20	95	98	Trace	25	
	90	20	20.4	10	N.o.	20	
	20 ^l	20	46	71	N.o.	28	

^aNot determined if not given; n.o. = not observed. ^bBased on CHD. ^cBased on the ET reagent and calculated for a two-electron process. ^dHeterogeneous system. ^eReaction period 24 h. ^f Bu_4NPF_6 (0.1 M) added; reaction period 3 h. ^gConditions: 22 h at 20°C, followed by 24 h at 40°C. ^hTraces of chloro products ($\text{HCl} + \text{CHD}$, $\text{HCl} + \text{dimers}$) and oligomers were detected. ⁱImmediate color change. ^jChloro products ($\text{HCl} + \text{CHD}$, 2% and $\text{Cl}_2 + \text{CHD}$, 17%) were formed. ^k2,6-Di(*tert*-butyl)pyridine (1.2 equiv.) was added. ^lCHD was added dropwise.

Table 5. GLC-detectable products from the reaction of CHD (24 mM) with aromatic radical cations (ArH^{•+}, 1.2 mM) in dichloromethane^a/Bu₄NPF₆ (0.1 M). For E° values, see Ref. 33.

Reaction conditions			Yield (%) of			Color change
ArH (E°/V vs. SCE)	Temp./°C	Reaction period/min	Recovered CHD	DA dimers ^b (endo/exo)	Benzene ^c	begin → end (time/min at 20 °C)
Thianthrene (1.28)	20	≤0.5	52	35 (5.6)	16	Purple → colorless (≤0.5)
	0	≤0.5	35	57 (5.4)		
	0 ^d	≤0.5	5.4	79 (6.2)	13	
	-20	≤0.5	45	48 (4.7)		
	-20	15	43	46 (4.5)		
9,10-Diphenylanthracene (1.20)	20	5	70	26 (4.9)	50	Blue → yellow 02)
	0	15	45	55 (4.9)	39	
Tris(4-bromophenyl)amine (1.06)	20	7	45	55 (5.6)	27	Blue → light green (7)
	0	15	56	45 (5.5)		
9,10-Dimethylantracene (0.87)	20	120	0	5 (4.8)		Green → purple-brown (120)
Tris(4-tolyl)amine (0.75)	20	1260 ^f	74 ^g	3 (5.3)		Blue → purple ^{h,i}
N-Methylphenothiazine (0.70)	20	1020	90	0.5	60	Purple → light green ⁱ (1020)
Tris(4-anisyl)amine (0.52)	20	1440 ^f	76 ^g			Blue → blue-purple ^{h,i} (1440)

^aDichloromethane/TFA/TFAA (97/2/1) for thianthrene and 9,10-diphenylanthracene, dichloromethane/TFA (95:5) for 9,10-dimethylantracene. ^bBased on CHD. ^cBased on ArH^{•+} and calculated for a two-electron process. ^d[ArH^{•+}] = 4.4 mM. ^eThe color disappeared within 0.5 min but the reaction mixture was left for 15 min. ^fQuenched after this period. ^gThe addition product (ca. 25 % yield) between CHD and ArH was also detected (see the text). ^hThe solution became light green upon quenching. ⁱEvolution of gaseous acid and etching of the reaction vessel was observed.

lites. It should be noted that Brønsted acid sites are formed³⁰ during reduction of the Cu^{II}Y zeolite which might cause oligomer formation.

Aromatic radical cations as catalysts. The triarylammonium ions, particularly the 4,4',4''-tribromo derivative, have commonly been regarded as outer-sphere ET oxidants.^{31,32} Our studies of the electrophilic properties of tris(4-bromophenyl)aminium ion toward charged nucleophiles^{4,6,7} however indicate great similarities to other aromatic radical cations. Thus TBPA^{•+} may not be unique as a catalyst for the DA dimerization reaction, but instead derive its popularity from the attractive property of giving a very stable (and commercially available) salt with hexachloroantimonate as the counterion. The aromatic compounds included here, thianthrene (TH), 9,10-diphenylanthracene (9,10-DPA), 9,10-dimethylantracene (9,10-DMA) and N-methylphenothiazine (N-MePT) were prepared by anodic oxidation in dichloromethane solution and used directly in the reactions with CHD. The results are summarized in Table 5.

Th^{•+} and (9,10-DPA)^{•+}, with redox potentials ≥ 1.20 V, were comparable to TBPA^{•+} in giving 50%, or better, yields of DA dimers when reactions were run under similar conditions. When TBPA^{•+} originated from the hexachloro-

antimonate salt,⁴ the yield was higher, 88%, with or without addition of tetrabutylammonium hexafluorophosphate. This difference is most likely caused by the presence of hexachloroantimonate ion in the latter case, since the choice of counterion is crucial for the outcome of the DA dimerization reaction (see below). Also, the formation of benzene from electrochemically prepared TBPA^{•+} (PF₆⁻ as the counterion), may be the result of the influence of the counterion.

9,10-DMA^{•+}, a weaker oxidant than TBPA^{•+} by ca. 0.2 V, gave a very low yield of DA dimers, and besides caused complete disappearance of the substrate. Presumably this is due to the relatively high acidity of radical cations of methylarenes,^{22,34,35} making protonation of CHD and subsequent polymerization possible. Also, adduct formation followed by polymerization according to eqn. (5) is



feasible,³⁶ as indicated by the fact that only 10% of the 9,10-DMA was recoverable (GLC). A similar loss was observed with Th^{•+} as the catalyst; only 50–70% was recovered in the experiments conducted at 0 °C. At the same time 10–15% CHD was missing in the GLC analysis, pointing to a CHD/Th ratio of 3–4 in any possible oligomer.

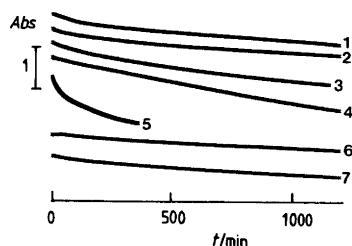
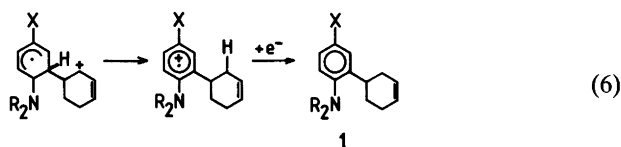


Fig. 2. Absorbance at 728 nm of 0.35 mM solutions of $\text{TBPA}^+\text{SbCl}_6^-$ in dichloromethane at 20.0 °C as a function of time in the presence of 0.35 mM Bu_4NX . The traces correspond to $\text{X}^- = 1, \text{PF}_6^-; 2, \text{BF}_4^-; 3, \text{ClO}_4^-; 4, \text{CF}_3\text{SO}_3^-; 5, \text{TsO}^-; 6, \text{none}; 7, \text{SbCl}_6^-$. Traces 1–4, 6 and 7 begin at $\text{Abs} \approx 2.4$ and 5, at ≈ 1.4 .

Similarly with $[\text{tris}(4\text{-methoxyphenyl})\text{amine}]^{++}$ as the catalyst (completely inactive for DA dimerization) both amine and substrate were partially missing in the GLC analyses. Again one might suspect that formation of oligomers via initiation by eqn. (5) is responsible, but being aware of the propensity of triarylaminium ions to react by substitution with nucleophiles,^{6,7} we also searched for possible products of this type. High-temperature GLC/MS analysis detected the presence of a substrate/amine coupling product (yield $\approx 20\%$). MS analysis indicated it to be an addition product between triarylamine and CHD ($M^+ = 415$). This might be formed via initial bonding between Ar_3N and CHD, followed by a hydride shift and subsequent reduction of the new radical cation [by Ar_3N ; see eqn. (6)]. A sigmatropic 1,3-hydrogen shift at the



- 1a: $\text{X} = \text{CH}_3\text{O}$, $\text{R} = 4\text{-CH}_3\text{OC}_6\text{H}_4$
 1b: $\text{X} = \text{CH}_3$, $\text{R} = 4\text{-CH}_3\text{C}_6\text{H}_4$

radical cation stage has been proposed in the DA dimerization of 1-acetoxy-1,3-cyclohexadiene.³⁷ Attempts to isolate **1a** by a combination of silica gel and alumina chromatography so far have failed owing to the instability of the compound.

An analogous addition product (**1b**) was formed and detected by GLC/MS using $[\text{tris}(4\text{-tolyl})\text{amine}]^{++}$ as the catalyst; again it was not possible to separate this material from the triarylamine.

Salt effects. In numerous reports Koshechko *et al.*^{38–44} have examined the influence of electronic structure of the radical cation, its counterion and the solvent upon reactions of triarylaminium ions. Observations of the complete inhibition of catalytic reactions of TBPA^+ with perchlorate as counterion^{37,45} prompted us to study the effect of the counterion on the TBPA^+ -catalyzed DA dimerization of CHD.

We first established that $\text{TBPA}^+\text{SbCl}_6^-$ solutions in dichloromethane undergo very slow decrease in $[\text{TBPA}^+]$ (ca. 30% over a period of 20 h; see Fig. 2) alone or in the presence of excess hexachloroantimonate ion (supplied as the tetrabutylammonium salt). Similarly, very slow decays were noted in the presence of equal concentrations of perchlorate, trifluoromethanesulfonate, tetrafluoroborate and hexafluorophosphate ion, whereas *p*-toluenesulfonate (tosylate) ion led to a somewhat faster decay (ca. 80% over 6 h; Fig. 2). These ions are commonly assumed to be of the 'inert' type.

These reactions were negligibly slow in relation to the rapid disappearance of the radical cation in the presence of CHD. With $\text{TBPA}^+\text{SbCl}_6^-$ (0.31 mM) and CHD (6.0 mM) alone, a pseudo-first-order rate constant of $3.5(1) \text{ min}^{-1}$ at 20.0 °C was determined. Since the kinetics actually are much more complex,⁴ this value should only be employed as a calibration mark for comparison with the rate constants reported below in the presence of 'inert' anions.

The blue color of $\text{TBPA}^+\text{SbCl}_6^-$ disappeared completely within seconds when the salt (0.31 mM) was added to a solution containing tetrabutylammonium perchlorate (0.31 mM) and CHD (6.0 mM). This decay followed first-order kinetics with $k = 19(1) \text{ min}^{-1}$ [Fig. 3(a)]. After a few minutes, the blue color slowly reappeared, eventually reaching an absorbance of ca. 0.15 at 634 nm. A run at twice the concentration level shows this feature much more

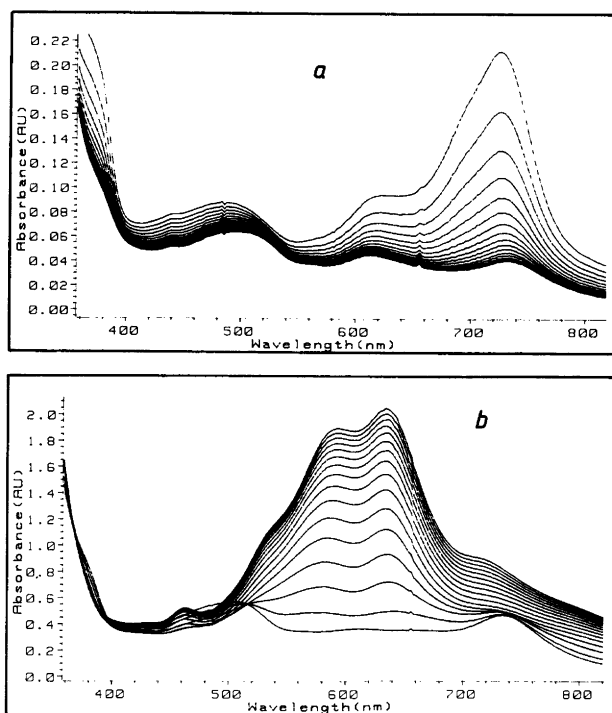


Fig. 3. (a) Repeated scans at 2 s intervals, the first spectrum being recorded 6 s after mixing (stopped-flow). $[\text{TBPA}^+]_0 = 0.31 \text{ mM}$; $[\text{Bu}_4\text{NClO}_4]_0 = 0.30 \text{ mM}$; $[\text{CHD}]_0 = 6.0 \text{ mM}$. (b) Repeated scans at 100 s intervals, the first spectrum being recorded 20 s after mixing. $[\text{TBPA}^+]_0 = 0.57 \text{ mM}$; $[\text{Bu}_4\text{NClO}_4]_0 = 0.61 \text{ mM}$; $[\text{CHD}]_0 = 11.8 \text{ mM}$. The solvent was dichloromethane and temperature 20.0 °C.

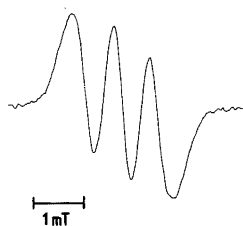


Fig. 4. ESR spectrum recorded ca. 40 min after mixing of solutions according to the experiment of Fig. 3(b). The same spectrum was also obtained in the absence of the perchlorate salt.

clearly [Fig. 3(b)]; absorbance with maxima at 580 and 634 nm and shoulders at ca. 515 and 710 nm builds up with a first-order rate constant of 0.40 min^{-1} to a maximum concentration, and this blue color eventually fades with a first-order rate constant of 0.0087 min^{-1} . Since it was suspected that the new blue color might be associated with the formation of radicals, the solutions were monitored by ESR spectroscopy. Indeed an ESR signal (Fig. 4) developed, reached a maximum after ca. 40 min and then slowly decayed. However, the decay was significantly slower than that of the blue color, the ESR signal persisting to an extent of $\approx 25\%$ of its maximum amplitude after 50 h (giving $k \approx 5 \times 10^{-4} \text{ min}^{-1}$). A blind check of a reaction run without perchlorate present showed that the same ESR signal developed and persisted for a long period. This novel feature of the TBPA^{++} -catalyzed DA reaction will be investigated later.

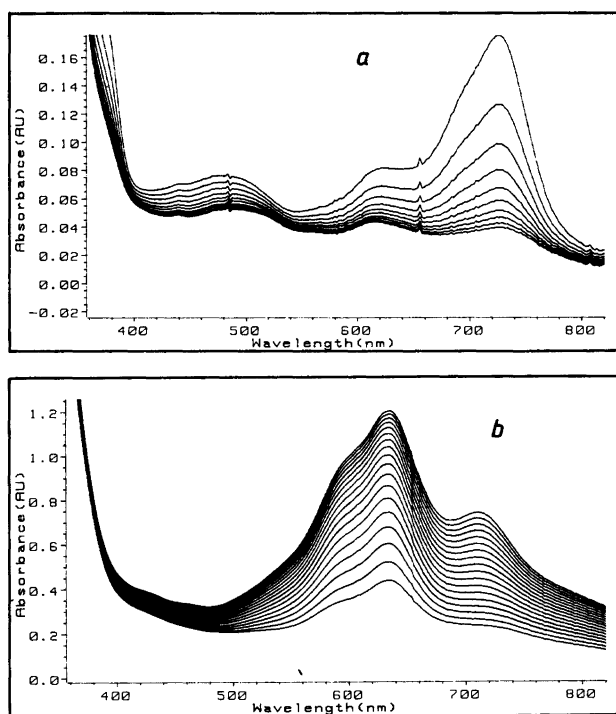


Fig. 5. (a) Repeated scans at 2 s intervals, the first spectrum being recorded 5 s after mixing (stopped-flow technique). $[\text{TBPA}^{++}]_0 = 0.31 \text{ mM}$; $[\text{Bu}_4\text{NCF}_3\text{SO}_3]_0 = 0.30 \text{ mM}$; $[\text{CHD}]_0 = 6.0 \text{ mM}$. (b) Repeated scans at 120 s intervals, the first spectrum being recorded 600 s after mixing. $[\text{TBPA}^{++}]_0 = 0.62 \text{ mM}$; $[\text{Bu}_4\text{NCF}_3\text{SO}_3]_0 = 0.60 \text{ mM}$; $[\text{CHD}]_0 = 11.8 \text{ mM}$. Solvent was dichloromethane and temperature 20.0°C .

Trifluoromethanesulfonate under the same conditions behaved similarly (Fig. 5), in that the first decay of $[\text{TBPA}^{++}]$ followed a rate constant of $22(1) \text{ min}^{-1}$, the build-up of the new blue color took place with $k = 0.068 \text{ min}^{-1}$ and its decay with $k = 0.0088 \text{ min}^{-1}$. The shape of the spectrum of the new blue species was slightly different [cf. Fig. 3(b) and 5(b)].

Similar experiments with hexafluorophosphate, tetrafluoroborate or tosylate ion demonstrated fast decay of $[\text{TBPA}^{++}]$ [$k = 12.1(4)$, $21.0(6)$ or $44(1) \text{ min}^{-1}$], but in these cases no new blue color developed, even over a period of 20 h.

Table 6 shows that the addition of perchlorate or trifluoromethanesulfonate strongly inhibits the formation of DA dimers and favors the formation of benzene. An experiment run over long periods of time shows that $\approx 50\%$ of the DA dimerization reaction took place in the first 15 min and that the rest was formed during the period where the new blue species was present. Most or all of the benzene was formed during the first 15 min. With trifluoromethanesulfonate present, the whole reaction is over in 15 min. Tosylate almost completely inhibited the reaction, as expected from consideration of Fig. 2. The initial reaction (first few min) between tosylate and TBPA^{++} lowers $[\text{TBPA}^{++}]$ to levels below which it does not sustain the DA dimerization reaction.¹⁷

Discussion

At the outset, we note that the catalytic role of TBPA^{++} in DA dimerization commonly is described in terms of outer-sphere electron transfer (ET).¹ The initial step is considered to be the ET equilibrium [eqn. (1)], followed by coupling of the substrate radical cation [eqn. (2)] with a parent molecule and chain transfer [eqn. (3)], or alternatively reduction by TBPA [eqn. (4)],^{3,4} the best reductant of the system. This mechanism has attractive features; it is simple, conforms with other ET-catalyzed mechanisms and explains many experimental findings.

However, a proper ET mechanism should be extendable to other ET reagents of a different nature, for example purely inorganic reagents of the outer-sphere type. Table 8 summarizes the essential features of the catalytic properties of the reagents studied above. To begin with radical cations other than TBPA^{++} , those with an E° above that of TBPA^{++} efficiently catalyze the DA dimerization of CHD, whereas those with lower E° do not support the reaction; instead, what presumably are adducts (**1a, b**) are formed from the triarylammonium ions. This means that the electrophilic reactivity of Ar_3N^{++} takes over in these cases. This is not so surprising, since ET from CHD would be energetic by 0.91 and 1.14 eV, respectively, for these triarylammonium ions.⁴ On going to the typical outer-sphere ET reagents, WCl_6 , OsCl_6^- and $\text{Ce}(\text{NO}_3)_6^{2-}$, all of high oxidizing power on a par with or stronger than that of TBPA^{++} , a surprising result emerges; they do not support DA dimerization but produce benzene and/or cause polymerization. Benzene is

Table 6. GLC/MS detectable products (see also Table 7) formed in the reaction between TBPA⁺⁺ SbCl₆⁻ (0.8 mM) and CHD (16 mM) in dichloromethane at 20 °C, with different Bu₄N⁺X⁻ (0.8 mM unless otherwise stated) added.

Reaction conditions		Yield (%) of			Colour at the end of the reaction ^c
X ⁻	Reaction period/h	Recovered CHD	DA dimers ^a (<i>endo/exo</i>)	Benzene ^b	
None	0.25	12	82 (6.2)		Green
ClO ₄ ⁻	0.25	66	5 (5.3)	30	Blue [Fig. 3(b), 5(b)]
	1.5	58	8 (5.1)	32	
	4	57	9 (5.2)	34	
	8	58	10 (5.3)	34	
	21.5	61	10 (5.0)	39	
	72	58	8 (5.2)	37	
ClO ₄ ^{-d}	0.25	64	17 (5.1)	30	Blue
ClO ₄ ^{-e}	0.25	43	55 (5.5)	38	Light brown
PF ₆ ⁻	0.25	19	81 (5.8)		Light green
PF ₆ ^{-f}	0.25	8	82 (6.2)		Light black-brown
BF ₄ ⁻	0.25	54	47 (6.1)	14	Light brown ^g
	4	46	44 (6.3)	21	Light brown ^g
CF ₃ SO ₃ ⁻	0.25	63	9 (5.5)	50	Blue-purple
	1	61	10 (5.3)	60	
	16	54	10 (5.5)	68	
TsO ⁻	0.25	98	1		Light brown

^aBased on CHD. ^bBased on TBPA⁺⁺ and calculated for a two-electron process. ^cBefore addition of CHD, the solutions were blue.

^d[ClO₄⁻] = 0.4 mM. ^e[ClO₄⁻] = 0.1 mM. ^f[PF₆⁻] = 100 mM. ^gLight green after first 2 min.

the primary product expected from ET oxidation of CHD in a non-nucleophilic medium like dichloromethane. On the other hand, Fe(III)(phen)₃³⁺, assumed to be an outer-sphere ET oxidant,¹⁹⁻²² gives high yields of the DA dimers.

Ferric chloride, in both hydrated and anhydrous forms, represents formally the class of Lewis acids but in addition is an oxidant, at least in its anhydrous state.⁵⁰ It supports oxidative chlorination and different dehydrodimerization modes of aromatic hydrocarbons and it has been assumed that these reactions are of the ET type. It may not therefore be so surprising that anhydrous iron(III) chloride, a strong oxidant, catalyzes DA dimerization. What is less easily explained is why its hydrated forms, of considerably lower redox reactivity, can still catalyze the reaction. Aluminium chloride, a reagent of choice for the generation of aromatic radical cations,⁵¹ might be an inferior catalyst for

DA dimerization because of its inability to sustain an Al(II) state for donating an electron back to a radical cation.

From the above considerations the contours of an alternative mechanism can be envisioned: instead of fully developed ET steps involving free radical cations, we propose that the catalyst functions in an inner-sphere type mechanism in which bonding between the catalyst and the substrate [as in eqn. (5)] controls the outcome of the dimerization process. Differently phrased, the radical

Table 8. Overview of the catalytic properties vs. DA dimerization of CHD of reagents described in the text. For E° values of radical cations, see compilation in Ref. 33.

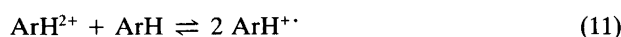
Reagent	E°/V vs. SCE	Yield of DA dimers (%)	Yield of benzene (%)
Protic acid TFA		15	—
FeCl ₃ · 2.5 H ₂ O		70	1
FeCl ₃ · 6 H ₂ O		38	1
FeCl ₃	>1.2 ⁴⁶	66	5
AlCl ₃	>1.2 ⁴⁷	4	6
TiCl ₄		1	4
SnCl ₄		4	1
Fe(CN) ₆ ³⁻	-0.6 ⁴⁸	0	0
Fe(III)(phen) ₃ ³⁺	0.98 ¹⁷	84	—
Co(III)W ₁₂ O ₄₀ ⁵⁻	0.15 ²³	—	—
WCl ₆	1.7 ⁴⁹	16	10
OsCl ₆ ⁻	1.20 ²⁵	2	11
Ce(NO ₃) ₆ ²⁻	0.95 ²⁶	Trace	25
Th ⁺⁺	1.28	79	13
(9,10-DPA) ⁺⁺	1.20	55	39
TBPA ⁺⁺	1.05	55	27
(9,10-DMA) ⁺⁺	0.87	5	—
(4-CH ₃ C ₆ H ₄) ₃ N ⁺⁺	0.71	3	—
N-MePT ⁺⁺	0.70	1	69
(4-CH ₃ OC ₆ H ₄) ₃ N ⁺⁺	0.52	—	—

Table 7. Addition products detected by GLC/MS in the reaction between TBPA⁺⁺ SbCl₆⁻ (0.8 mM) and CHD (16 mM) in dichloromethane at 20 °C, with different Bu₄N⁺X⁻ (0.8 mM) present.

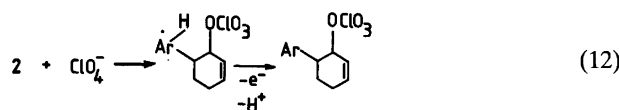
X ⁻	Addition products		
	CHD + HCl m/z = 116	CHD + Cl ₂ m/z = 150	Open-chain CHD dimers m/z = 160
None		×	
ClO ₄ ⁻	×	×	×
PF ₆ ⁻			
BF ₄ ⁻	×	×	
CF ₃ SO ₃ ⁻	×	×	×
TsO ⁻			
HSO ₄ ⁻			

^aAlso CHD + HF addition product was detected.

cation plays the role of an electrophile, and ET provides the driving force for the bond cleavage necessary to set the DA dimer free. Such a mechanism is exemplified in eqns. (7)–(11). In eqn. (7) ArH^{2+} electrophilically attacks a double



bond in CHD, forming a distonic⁵² radical cation (2) whose double bond is strongly activated towards cycloaddition of a second CHD [eqn. (8)]. A second distonic ion (3) results and this bears the same relation to $(\text{CHD})_2$ as 2 does to CHD. In order to cleave off the ArH moiety, 3 must be oxidized to the dication 4, from which ArH^{2+} is cleaved off and $(\text{CHD})_2$ is liberated. ArH^{2+} then immediately disproportionates with ArH, thus reforming the original catalyst ArH^+ . The last step explains the kinetic inhibition caused by added ArH.^{2,4} The mechanism of eqns. (7)–(10) corresponds to the well-known half-regeneration mechanism.³² This mechanism neatly explains the formation of adducts [eqn. (6)] for the less active radical cations; the 1,3-hydride shift in 2 competes with CHD addition to the double bond. Also the effects of added 'inert' salts can be rationalized by noting that some of these are not as innocent chemically as generally assumed. Perchlorate and trifluoromethanesulfonate are known^{53,54} to react with cationic centers under conditions where ion pairs control the reactivity of the participating species. Thus one might surmise that 2 reacts with these ions according to eqn. (12); eventually leading



to covalent, colorless compounds. These will, however, be unstable toward solvolysis⁵⁵ and will decompose (formation of the new blue color) more or less rapidly. With truly inert anions, like SbCl_6^- , PF_6^- and possibly BF_4^- , no covalent bonding to 2 is possible and thus DA dimerization becomes predominant. The failure of hexachloroosmate(V) and

hexanitratocerate(IV) to catalyze DA dimerization is explained by their reluctance to form a bond to CHD, whereas iron(III) compounds may not cause difficulties in this respect, given that the electrophilic reactivity is high enough.

We do not claim that this study has solved once and for all the mechanistic problems related to the radical cation catalyzed Diels–Alder reaction. It has, however, clearly demonstrated that other types of catalyst sustain this reaction and that electrophilic mechanisms should be seriously considered in view of the inconsistencies generated by the outer-sphere ET hypothesis. One catalyst of possibly different nature, iron(III) chloride should be of interest for further exploration because of its effectiveness and cheapness.

Experimental

General methods. Most of these have been described in previous papers.^{4,6,7} Stopped-flow measurements were performed at 20.0°C, using the Rapid Kinetics Spectrometer Accessory (Model RX.1000, cell path 2 mm) from Applied Photophysics, Leatherhead, England in conjunction with an HP 8452A diode-array spectrophotometer and HP 89500 UV/VIS ChemStation. Kinetic runs and data treatment were performed by means of the HP 89512 Kinetics Software. EPR spectra were recorded on a Bruker ER-200D SRC instrument. Response factors for GLC analysis were determined for CHD, benzene and DA dimers; for other products they were put equal to 1.00.

Materials. The reagents tris(phenanthroline)iron(III) hexafluorophosphate,¹⁹ tetrabutylammonium hexanitratocerate(IV),⁵⁶ tetrabutylammonium 12-tungstocobaltate(III),⁵⁷ tetraphenylphosphonium hexachloroosmate(V),⁵⁸ tetrabutylammonium hexachloroantimonate,⁴ 10-methylphenothiazine,⁵⁹ tris(4-methoxyphenyl)amine⁶ and tris(4-tolyl)amine⁶⁰ were prepared and purified according to the references given. Cu^{II}Y was made from NaY zeolite by means of ion exchange. Tetrabutylammonium hexafluorophosphate was recrystallized twice from ethyl acetate/cyclohexane (7/3). Dichloromethane (Merck AG, Darmstadt, Germany: *zur Rückstandsanalyse*) was stored over 3 Å molecular sieves. Other chemicals used were of highest commercial quality available.

Catalysis by Brønsted acids. Solutions of CHD were kept at the desired temperature and the acid was added to give a total volume of 25 ml. Water (15 ml) was added to stop the reaction where upon the color of the solutions disappeared. After the solution had been washed with saturated sodium hydrogencarbonate solution, an internal standard was added and analysis performed either (in cases where analysis for recovered CHD was desired) by passing the solution through a short column of silica gel, followed by GLC analysis by capillary GLC/MS (25 m × 0.25 mm OV-1701 column) or (in all other cases) by GLC/MS (3 m × 3 mm

OV-101 3% column). The DA dimers were stable under conditions where TFA was used as a catalyst.

Catalysis by iron(III) chloride. The iron salt was added to 25 ml of dichloromethane and CHD was added via a syringe to the rapidly stirred mixture, kept at the appropriate temperature. The reaction was allowed to proceed for 15 min. An internal standard was then added and GLC analysis performed as described above. The addition products between dimers and HCl or Cl₂ most likely possess acyclic structures (GLC/MS). Three products with $M^+ = 230$, i.e., dimer + Cl₂, were formed and a typical mass spectrum was as follows [m/z (rel. intensity)]: 230 (M^+), 232 (3.4), 230 (5.4), 197 (2.6), 195 (8.0), 159 (7.6), 134 (100), 133 (32), 119 (14), 117 (13), 105 (15), 91 (61), 79 (82), 77 (46), 67 (21), 65 (17), 53 (17), 41 (38).

Catalysis by other inorganic ET reagents. The reactions with soluble reagents were performed and analyzed as described above and earlier.⁴ The zeolite [500 mg of Cu^{II}Y \approx 0.75 mmol of Cu(II)] was suspended in 10 ml of solvent. CHD (0.90 mmol) was added by syringe and the reaction was allowed to proceed for 15 min. An internal standard was added and the solution was passed through a short silica gel column. Afterwards 15 ml of dichloromethane were passed through the column and GLC analysis performed as before on the resulting solution.

Catalysis by aromatic radical cations. The aromatic compound (0.060 mmol) in electrolyte (50 ml) was electrolyzed until 1 F mol⁻¹ of charge had been passed in a three-compartment cell, using a Pt foil anode (10 cm²) and a Pt wire cathode. The anode potential was kept constant (vs. an Ag wire) at the value required for current starting to pass through the solution at 0.6 mA cm⁻². Depending on the stability of the radical cation formed, the solvent was chosen as follows: for thianthrene and 9,10-diphenylanthracene dichloromethane/TFA/TFAA (97/2/1), for 9,10-dimethylanthracene dichloromethane/TFA (95/5), and for the remainder dichloromethane alone. In all cases tetrabutylammonium hexafluorophosphate (0.1 M) was the supporting electrolyte. After electrolysis, CHD (0.60 mmol) was added to 25 ml of the solution. The reaction was allowed to proceed until the color of the radical cation had disappeared or until a defined time had elapsed, whichever was the shortest. In reactions with tris(4-tolyl)aminium or tris(4-methoxyphenyl)aminium ion the solution was quenched as described earlier.⁴ Internal standard was added and the solution was washed with saturated NaHCO₃ solution (if TFA had been used), passed through a short silica gel column and analyzed by GLC as before.

Detection of an addition product (1a) between CHD and tris(4-methoxyphenyl)aminium. Anodic oxidations and reactions were performed four times as before (twice with [Ar₃N] = 3 mM, [CHD] = 60 mM). The combined reaction mixtures were washed with water, dried and freed from

solvent by evaporation. The residue was extracted with diethyl ether. GLC/MS analysis showed a 60/40 mixture of unsubstituted/substituted amine. A shoulder on the slope of the substituted amine peak might be due to the presence of the substitution product (1a - 2 H). At this stage 1a was identified by GLC/MS analysis, MS [m/z (rel. intensity)]: 415 (M^+), 416 (19), 415 (75), 400 (8), 372 (7), 349 (32), 334 (100), 317 (5), 279 (6), 175 (8), 151 (9).

Identification of the addition product (1b) between CHD and tris(4-tolyl)amine. The reactions were performed as above. GLC analysis showed a ratio of unsubstituted/substituted amine of 70/30. The adduct 1b was preliminarily identified by GLC/MS analysis. MS [m/z (rel. intensity)]: 367 (M^+), 368 (24), 367 (100), 352 (12), 338 (4), 324 (22), 312 (4), 298 (12), 286 (5), 234 (12), 208 (15), 194 (10), 181 (6), 155 (9), 141 (9), 105 (17), 91 (14), 79 (8).

Reactions with tetrabutylammonium salts added. These were performed by dissolving TBPA⁺SbCl₆⁻ (0.8 mM) and Bu₄NX (0.8 mM) in 25 ml of dichloromethane at 20°C. CHD (16 mM) was added by syringe and the reactions were allowed to proceed for a fixed time period and analyzed by GLC as described before. To check the stability of the radical cation salt with Bu₄NX added, the absorbance of solutions, 0.35 mM in both components, was monitored at 728 nm for 6 (tosylate) or 20 h (remaining ions).

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