was washed and dried and the solvent removed to give 1.0 g of a crude 4:1 mixture of **36** and **35** which was obtained in 70% yield. This mixture was charged on a silica gel (20 g) column. Elution with 10% ethyl acetate–petroleum ether furnished the major enone **36**, 460 mg, bp 130 °C/0.2 torr, identical with the sample obtained in the previous experiment. Further elution of the column gave the minor enone **35**, 116 mg, bp 130 °C/0.2 torr, identical with the sample obtained in the previous experiment.

2,9α-Dimethyltricyclo[6.3.0.0^{4,8}]undec-2-en-6-one (39). To a solution of the enone **36** (350 mg, 2.0 mmol) in 4 mL of 85% formic acid, BF_3–etherate (0.2 mL) was added and the solution was heated for 2 h at 90 °C. The reaction mixture was cooled, slowly poured into ice-cold water, and extracted with ether (3 × 20 mL). The ethereal solution was washed with 5% $NaHCO_3$ and dried, and the solvent was removed to give 350 mg of oily residue which was charged on a silica gel (10 g) column. Elution with 2% ethyl acetate–petroleum ether furnished the tricyclic ketone **39**, 192 mg (55%), which distilled at 120 °C/0.3 torr: IR (neat) ν_{max} 3030, 2950, 1740, 920, 730 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.16 (1 H, br s), 3.32–2.96 (1 H, m), 2.9–1.12 (10 H, m), 1.68 (3 H, br s), 1.0 (3 H, d, J = 7 Hz). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.01; H, 9.62.

2,9α-Dimethyltricyclo[6.3.0.0^{4,8}]undec-2-ene-6-carboxaldehyde (40a). Into a 50-mL, three-necked, round-bottomed flask fitted with a dry N_2 inlet, septum, reflux condenser, and mercury seal was placed (methoxymethyl)triphenylphosphonium chloride (2 g, 6 mmol). The solid was suspended in 15 mL of dry ether, and freshly sublimed sodium *tert*-amyl oxide (430 mg, 3.9 mmol) in 5 mL of dry ether was added. The dark-red reaction mixture was stirred for 45 min at room temperature, to this the tricyclic ketone **39** (250 mg, 1.3 mmol) in 5 mL of dry ether was introduced, and reactants were stirred for 1 h. The reaction mixture was quenched with water and extracted with ether (4 × 20 mL). The ethereal layer was washed and dried, and the solvent was removed. The crude reaction mixture was used as such for the next step.

The crude reaction mixture obtained above was dissolved in 10 mL of ether, and to this 8–10 drops of 35% perchloric acid (ice bath) were added. The reaction mixture was stirred for 18 h at room temperature, diluted with ether, and quenched with 5% $NaHCO_3$. The ethereal layer was washed and dried. The residue obtained after removal of the solvent was filtered through a silica gel (10 g) column. Elution with petroleum ether resulted in the removal of triphenylphosphine-derived impurities, and further elution with 25% benzene–petroleum ether furnished the aldehyde **40a** (mixture of aldehyde epimers): 208 mg (80%); IR (neat) ν_{max} 3030, 2950, 2700, 1720, 1440 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 9.53 (1 H, br s), 4.98 (1 H, br s), 3.3–1.2 (12 H, series of m), 1.53 (3 H, m), 0.93 (3 H, d): exact mass calcd (M^+) 204.27, found 204.0.

2,6,9α-Trimethyltricyclo[6.3.0.0^{4,8}]undec-2-ene-6-carboxaldehyde (40b). Potassium hydride (140 mg, 24% wt dispersion in oil, 0.87 mmol) was placed in a 25-mL, three-necked flask equipped with a magnetic pellet, dry N_2 inlet, and septum. The mineral oil was twice washed with dry petroleum ether and the residue suspended in 2 mL of dry THF. A solution of aldehyde **40a** (120 mg, 0.58 mmol) in 2 mL of dry THF was added dropwise at −5 °C. After 2 min the reaction was quenched with MeI (0.1 mL, freshly distilled over $CaCl_2$) and further stirred for 4 h at 5–10 °C. The reaction mixture was diluted with water and extracted with ether (3 × 10 mL). The ethereal extract was washed and dried, and removal of solvent gave crude cis-aldehyde **40b**, 133 mg. Filtration through a silica gel (10 g) column, with 50% benzene–petroleum ether furnished the C_{15}-aldehyde **40b** (mixture of aldehyde epimers): 79 mg (63%); IR (neat) ν_{max} 3030, 2950, 2700, 1720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 9.51 (2 H, br s), 4.96 (2 H, br s), 3.13–1.25 (28 H, series of m), 1.0–0.9 (12 H, m); exact mass calcd (M^+) 218.29, found 218.0.

(±)-*epi*-Pentalenene (10). A mixture of C_{15}-aldehyde **40b** (36 mg, 0.16 mmol), 1.5 mL of ethylene glycol, 6 mL of diethylene glycol, and hydrazine hydrate (20 mg, 99%, 0.4 mmol) was heated to 180 °C for 1.5 h. After the mixture cooled to 70 °C, sodium (10 mg, 0.45 mmol) in 1 mL of diethylene glycol was added, and the reaction mixture was heated under reflux for 4 h. The reaction mixture was poured into ice-cold water and extracted with pentane (4 × 10 mL). The pentane layer was washed and dried. The residue obtained after removal of solvent was filtered through a silica gel (5 g) column. Elution with pentane furnished *epi*-pentalenene (**10**): 12 mg (33%); ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.14 (1 H, br s), 2.86 (1 H, m), 2.58 (1 H, m), 1.6 (3 H, m), 1.73–0.86 (18 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 140.6, 131.3, 63.4, 54.7, 50.5, 46.1, 45.0, 39.6, 32.9, 31.4, 28.5, 29.2, 15.3, 13.5. This was found identical with the comparison spectra provided by Prof. Paquette.

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Registry No. (±)-**6**, 82442-49-7; (±)-**10**, 82398-57-0; (±)-**11a**, 104762-08-5; (±)-**11b**, 104762-13-2; (±)-**16**, 104762-06-3; (±)-**17**, 104762-07-4; **18**, 637-90-1; (±)-**19**, 104762-11-0; **19**-ol, 104762-10-9; (±)-**20**, 104762-12-1; (±)-**21**, 104762-14-3; **22**, 92590-08-4; (±)-**23**, 104833-04-7; **23**-ol, 104762-09-6; (±)-**27** (isomer 1), 104762-15-4; (±)-**27** (isomer 2), 104833-05-8; **28**-ol, 104762-16-5; **28**, 104762-17-6; (±)-**30**, 104762-18-7; (±)-**31**, 104762-19-8; (±)-**32**, 101366-64-7; (±)-**33**, 101366-65-8; (±)-**34**, 101366-66-9; (±)-**35**, 101366-67-0; (±)-**36**, 101366-68-1; (±)-**37**, 101383-50-0; (±)-**37** (methoxymethylene derivative), 104762-20-1; (±)-**38a** (isomer 1), 104833-06-9; (±)-**38a** (isomer 2), 104833-07-0; (±)-**38b** (isomer 1), 104833-08-1; (±)-**38b** (isomer 2), 104833-09-2; (±)-**39**, 104833-10-5; (±)-**39** (methoxymethylene derivative), 104833-11-6; (±)-**40a** (isomer 1), 104833-12-7; (±)-**40a** (isomer 2), 104833-13-8; (±)-**40b** (isomer 1), 104833-14-9; (±)-**40b** (isomer 2), 104833-15-0; 1,5-dimethyl-1,5-cyclooctadiene, 3760-14-3; allyl lithium, 3052-45-7.

The Triplex Diels–Alder Reaction of Indene and Cyclic Dienes

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Abstract: Irradiation of 1,4-dicyanonaphthalene or 9,10-dicyanoanthracene in benzene solution containing indene and a cyclic 1,3-diene leads to isolation of Diels–Alder adducts in several cases. The mechanism of this reaction is proposed to proceed through formation of an intermediate exciplex of the dicyanoarene and indene. The exciplex combines with the diene to form a ternary complex (triplex) that leads eventually to the isolated cycloaddition products. This triplex reaction is compared with the recently popular radical cation and the well-known Lewis acid catalyzed Diels–Alder reactions.

The Diels–Alder reaction is one of the most important methods available for creation of carbon–carbon bonds and the formation of six-membered rings.[1] In the most favorable circumstances, when the diene and dienophile have strongly opposite electronic character, the reaction proceeds under mild conditions in excellent yield. In contrast, the Diels–Alder reaction of partners with similar electronic character often requires forcing conditions (high temperature or pressure) and usually results in only a poor to fair yield of the desired product. Recognition of this difficulty has led to the popularization of catalysis by Lewis acids in suitable cases[2] and to several attempts to find new ways to accelerate normally sluggish reactions.

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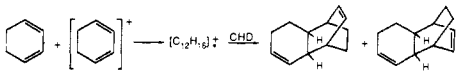
The radical cation Diels–Alder dimerization of 1,3-cyclohexadiene (CHD) was described first by Schenck and coworkers in 1964.[3] The mechanism of this reaction was later studied independently by Freeman[4] and Hammond.[5] Their results identified a process, initiated by γ radiation, that features addition of the CHD radical cation ($CHD^{\bullet+}$) to neutral CHD to generate a dimer radical cation ($C_{12}H_{16}^{\bullet+}$). The dimer radical cation is capable of oxidizing additional CHD and propagating a chain reaction that eventually gives the exo- and endo-[4 + 2] adducts characteristic of the Diels–Alder cycloaddition. This sequence is summarized in eq 1.



(1)

Additional examples of the radical cation Diels–Alder reactions have been reported since the early work on CHD. Arnold observed that the [4 + 2] dimerization of 1,1-diphenylethylene is initiated by photolysis of methyl *p*-cyanobenzoate in acetonitrile solution.[6] The radical cation of the ethylene was identified by flash photolysis, and it was shown that this intermediate could be diverted from the Diels–Alder path by methanol. Similar reactions of diphenylethylene with simpler alkenes as the dienophile component have been reported.[7]

Mizuno, Otsuji, and co-workers also investigated the photoinitiated radical cation Diels–Alder reaction.[8] They showed that irradiation of 1,4-dicyanonaphthalene (DCN) in the presence of indene (IN) and furan, for example, in polar solvents gives the [4 + 2] adduct in moderate yield. Preliminary analysis of the reaction mechanism implicates single electron transfer to excited DCN and the subsequent reaction of a radical cation to form the Diels–Alder adducts.

The [4 + 2] dimerization of phenylacetylene initiated by irradiation of tetracyanoanthracene in acetonitrile was observed by Farid and co-workers and attributed to a radical cation reaction.[9] In this case, different reactions are postulated to occur from the first-formed geminate ion pair and from the solvent-separated radical ions. A related suggestion was advanced to account for an unusual concentration dependence in the dimerization of diphenylethylene.[10]

A report in 1981 by Bauld and co-workers in which they claimed the discovery of the radical cation Diels–Alder dimerization of CHD refocused attention on this reaction.[11] In this version, the dimerization is initiated by tris(*p*-bromophenyl)aminium hexachlorostibnate which, despite a huge energy deficit, is presumed to oxidize CHD to the radical cation. Our work has confirmed some aspects of this sequence for CHD,[12] but experiments by Gassman and co-workers have cast doubt on the validity of Bauld's proposal in other cases.[13] Similarly, it has been reported recently that the aminium radical cation, generated electrochemically, does not initiate the reaction of a substituted cyclohexadiene that does not proceeed when the stibnate salt is used.[14]

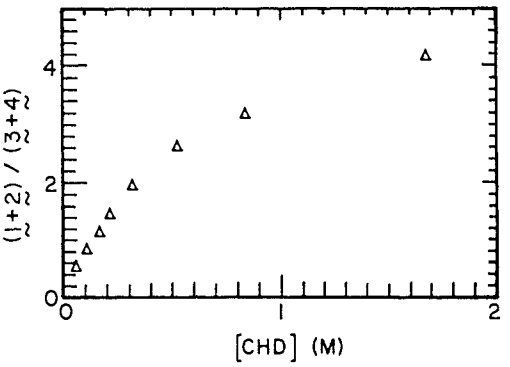


Figure 1. Dependence of the ratio of [4 + 2] to [2 + 2] cycloaddition for the DCN sensitized addition of IN to CHD.

A recent study by Laszlo and Lucchetti of the dimerization of CHD initiated by ferric ion trapped in a clay matrix also implicates the participation of a radical cation Diels–Alder chain mechanism.[15] The expected [4 + 2] cycloaddition products are obtained in good yield under mild conditions by a particularly convenient process.

It is well-known that reaction between electronically excited electron acceptors and olefins or dienes in nonpolar solvents often leads to detectable exciplex formation.[9,17] Intriguing reports from several groups suggest that there may be some parallel between the reactions of these exciplexes with dienes and the radical cation Diels–Alder cycloaddition.

Jones and co-workers observed that irradiation of dicyanoanthracene in a methylene chloride solution containing CHD gives the [4 + 2] dimers characteristic of the Diels–Alder reaction even though they believe that it should not be possible to form radical ions in this nonpolar solvent.[18] Formation of a ternary complex, triplex, was proposed to be a key step in this dimerization. Saltiel's group found that the quantum yield for dimerization of anthracene is enhanced by dienes and suggested that this comes about by capture of the anthracene–diene exciplex by a second anthracene molecule.[19a,b] However, more recent work by Kaupp and Teufer[19c] and a reinvestigation by Saltiel and co-workers[19d] have discounted this conclusion. A similar enhancement of 9-phenylanthracene dimerization by 1,3-pentadiene was observed by Campbell and Liu.[20] Yang and co-workers found that addition of 1,3-dienes to anthracene excimers leads to different products than does its addition to monomeric excited arenes.[21] Lewis and co-workers[22] found that stilbene excimers can be intercepted by dimethyl fumarate to give an oxetane through a presumed triplex.

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Scheme I

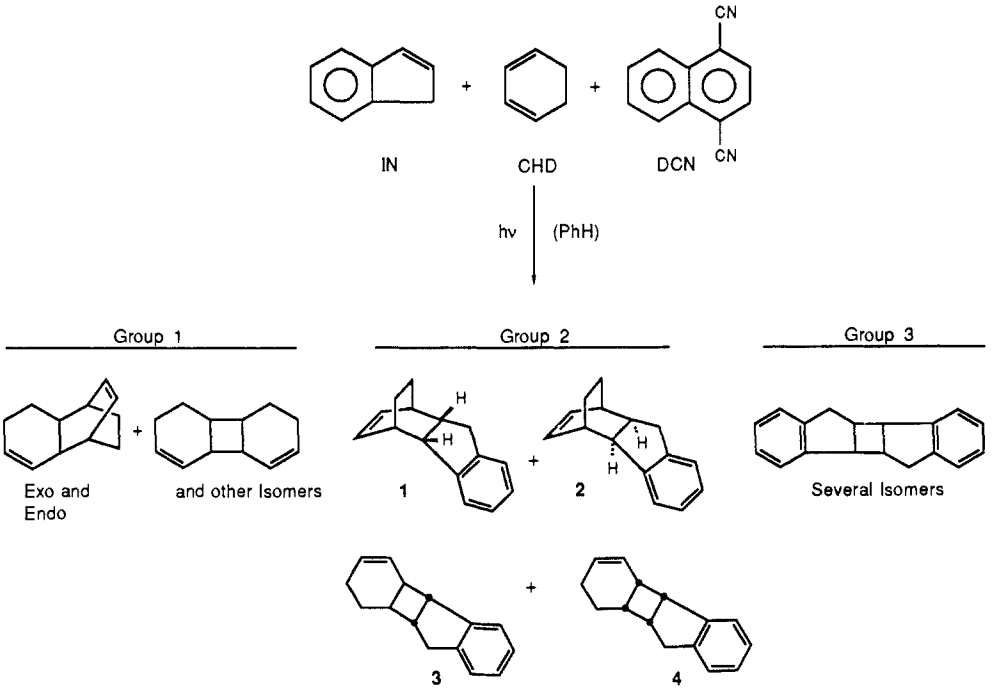

Table I.

			relative ratios[a]					
[CHD], M	[IN], M	Sens	group 1	**1**	**2**	**3**	**4**	group 3
0.10	0.11	DCN	41	5.2	2.4	2.8	1.0	0.7
0.21	0.11	DCN	74	7.0	3.2	3.0	1.0	0.4
0.32	0.11	DCN	110	7.3	3.3	2.8	1.0	0.3
0.52	0.11	DCN	170	8.4	3.9	2.7	1.0	
0.84	0.11	DCN	340	11	4.6	3.3	1.0	
1.10	0.11	DCN	330	9.7	4.3	2.9	1.0	
1.50	0.11	DCN	430	9.2	4.0	2.6	1.0	
2.10	0.11	DCN	700	9.5	4.0	2.3	1.0	
0.05	0.86	DCA	2	22.1	8.9	4.2	1.0	9.6
0.10	0.86	DCA	5	21.4	8.8	4.1	1.0	3.9
0.21	0.86	DCA	12	21.1	8.5	4.1	1.0	2.0
0.32	0.86	DCA	24	22.8	9.1	4.1	1.0	1.1
0.42	0.86	DCA	31	21.2	8.7	4.0	1.0	0.8
0.53	0.86	DCA	38	22.2	8.5	4.0	1.0	0.7
0.63	0.86	DCA	47	22.1	8.5	4.0	1.0	
0.84	0.86	DCA	67	21.8	8.7	3.9	1.0	

[a] Uncorrected for different response factors of the capillary gas chromatograph.

Herein we describe a Diels–Alder-like reaction of indene (the dienophile) with several cyclic 1,3-dienes that is initiated by irradiation of a dicyanoarene in benzene solution. The results reveal the existence of a novel, somewhat general, method for catalyzing the [4 + 2] cycloaddition of normally unreactive reagents.[23]

Results

(1) Addition of Indene to 1,3-Cyclohexadiene—Product Studies. Irradiation of a benzene solution of IN and CHD containing DCN through a uranium glass filter (only the DCN absorbs light) leads to formation of three sets of products. The first set consists of CHD dimers, the second is a group of adducts of IN to CHD, and the third is dimers of IN (Scheme I). The structures of these products were determined by comparison of their spectral and chromatographic properties with those of authentic samples independently prepared.[24,25] The assignment of endo stereochemistry to the major component of the IN to CHD [4 + 2] adduct rests on the presumption that the Alder rule is obeyed in the thermal addition of these compounds (as it is for the closely related addition of cyclopentadiene to indene)[25] and an analysis of the ^{1}H NMR spectra of the two bicyclo[2.2.2] isomers (see the Experimental Section).

The composition of the product mixture from this reaction is strongly dependent on the specific conditions. The highest yield of CHD to IN adducts (group 2 products) is obtained when the concentration of IN is high relative to that of CHD. The makeup of the group 2 adducts is similarly sensitive to the CHD concentration. The nature of these adducts changes from a mixture consisting of primarily [2 + 2] adducts (**3** and **4**) to one dominated by [4 + 2] adducts (**1** and **2**) as the concentration of CHD is increased from 0.05 to 1.7 M at constant IN concentration. This observation is illustrated graphically in Figure 1. Since both CHD and IN quench the fluorescence of DCN at a diffusion-controlled rate (vide infra), the mixture of the addition products obtained is dependent on both the relative and absolute concentrations of CHD and IN. The highest chemical yield of CHD to IN adducts is obtained at high relative IN concentration. The quantum efficiency for formation of the Diels–Alder adducts is 0.10 when the concentrations of IN and CHD are both ca. 0.85 M, and DCN is consumed slowly during the course of the reaction. The data are summarized in Table I.

The addition of IN to CHD follows a somewhat different track when 9,10-dicyanoanthracene (DCA) is the photosensitizer.

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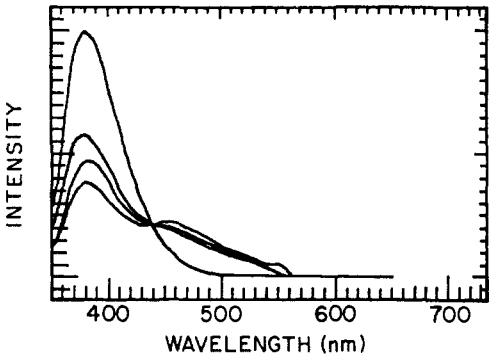

Figure 2. Emission of spectra of DCN, IN mixtures recorded in benzene solution at room temperature. The peak at λ_{max} = 382 nm is fluorescence of DCN; the broad peak with apparent maximum at 460 nm is assigned to the DCN–IN exciplex.

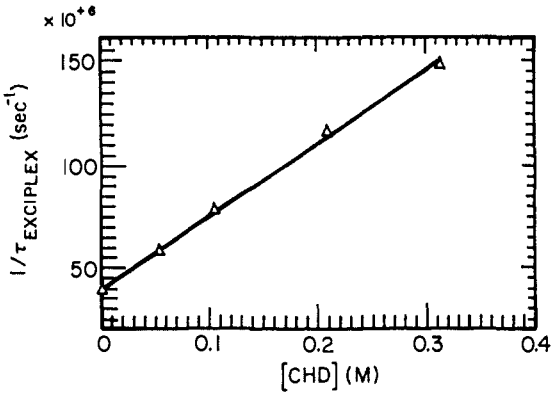

Figure 3. Quenching of the DCN–IN exciplex lifetime by CHD.

Irradiation of a benzene solution of DCA containing IN (0.86 M) and CHD (0.21) gives the three groups of products described above in a mole ratio of 4:13:1. However, the ratio of the [2 + 2] to the [4 + 2] adducts of IN to CHD [{**3** + **4**}/{**1** + **2**}] remains constant at ca. 1:6 regardless of the CHD concentration. A control experiment showed that **1** and **2** are not interconverted under the reaction conditions, nor do they revert to starting material. These data also are summarized in Table I.

For the purpose of comparison, the reaction of IN with CHD was also performed under classical triplet-sensitized conditions with 2-isopropylthioxanthone. In this case only three of the adducts of IN to CHD are obtained. Diels–Alder adduct **1** is not formed, and the ratio of the [2 + 2] to the [4 + 2] addition products [{**3** + **4**}/**2**] is 16:1. Clearly, the reaction caused by DCA or by DCN sensitization is not initiated by a simple triplet energy transfer.

The reaction to form the Diels–Alder adducts **1** and **2** can be carried out on a preparatively useful scale. Irradiation of a benzene solution (50 mL total volume) containing 4.8 g of IN, 840 mg of CHD, and 250 mg of DCA for 10 h with a 450-W lamp gives 620 mg of the [4 + 2] adducts after silica gel chromatography. The endo isomer is formed in excess (2.4:1). For comparison, the normal thermal Diels–Alder addition of IN to CHD requires 24 h at 200 °C and gives adducts **1** and **2** in a ratio of 15:1.

(2) Addition of Indene to 1,3-Cyclohexadiene—Photophysical Studies. The fluorescence of DCN is quenched at a rapid rate by both IN and CHD in benzene solution ($k_q\tau$ = 80 M^{-1}). It comes as no surprise that laser spectroscopy reveals no DCN radical anion formation in this reaction.[12] Separation of charge in a nonpolar solvent such as benzene is highly unfavorable. This observation rules out participation of an electron-transfer process and the formation of Diels–Alder adducts **1** and **2** by a radical cation route. Since the singlet energies of both IN and CHD are much greater than that of DCN, it is unlikely that simple singlet–singlet energy transfer is responsible for the quenching. Extensive investigation of the interaction between excited cyanoarenes and dienes by Yang and co-workers has revealed that exciplex formation occurs commonly in these systems.[21,26] These exciplexes sometimes are intermediates in the cycloaddition of the diene to the arene.

An exciplex between IN and excited DCN is readily detected in the emission spectra of benzene solutions containing both compounds (Figure 2). As the concentration of IN is increased, the fluorescence of DCN, centered at 382 nm, decreases and a new, broad emission with an apparent maximum at 460 nm grows into the spectrum. We assign this emission to the IN–DCN exciplex. No comparable exciplex emission is observed when DCN is quenched by CHD. The lifetime of the IN–DCN exciplex was measured by time-correlated single-photon counting. It is dependent on the concentration of IN in the solution (termolecular quenching, vide infra). At 1.7 × 10^{-2} M IN, the exciplex has a lifetime of 47.9 ± 0.9 ns. The lifetime of the residual DCN fluorescence under these conditions is 3.9 ± 0.8 ns. The finding of different lifetimes for these species is evidence that the exciplex is formed irreversibly.

The degree of charge transfer in an exciplex can be crudely estimated by determining the effect of solvent polarity on the energy of its emission.[27] The maximum of the IN–DCN exciplex shifts slowly red when the solvent is varied from nonpolar hexane through moderately polar dimethoxyethane (six solvents all together). A plot of this maximum against the usual solvent parameter indicates that the exciplex has a dipole moment of ca. 10 D (assuming a separation of 5 Å between two point charges). This corresponds to ca. 40% electron transfer from IN to DCN in the exciplex.

The fluorescence of DCN is completely quenched in benzene solutions containing 0.86 M IN, and only the emission of the exciplex is observed. The intensity of the exciplex emission decreases as CHD is added to this solution. Stern–Volmer analysis of this reaction reveals that the exciplex emission intensity does not decrease linearly with CHD concentration but follows a quadratic law ($\phi^0/\phi = 1 + 10.6[CHD] + 5.5[CHD]^2$) instead. This observation is consistent with the hypothesis that CHD quenches both DCN and DCN–IN exciplex fluorescence. Confirmation of this notion follows from the measurement of the exciplex lifetime as a function of CHD concentration (Figure 3). The slope in this plot of $1/\tau_{exciplex}$ against CHD concentration gives a rate constant for reaction of the exciplex with CHD of 3.5 × 10^8 M^{-1} s^{-1}. The quenching reaction must involve a termolecular complex of DCN, IN, and CHD (DCN–IN–CHD). Complexes of this sort have been observed previously and called triplexes or exterplexes.[28,29]

Quite similar photophysical results are obtained from the investigation of the DCA initiated reaction. Both IN and CHD quench the fluorescence of DCA at the diffusion-limited rate. In benzene solution an exciplex emission (λ_{max} = 510 nm) is seen with IN but not with CHD quenching. The lifetime of the exciplex is 46.5 ± 0.5 ns when the concentration of IN is 0.11 M. The DCA–IN exciplex is quenched by CHD. It should be noted that in the DCA–IN–CHD system, the species with lowest triplet energy is DCA. In contrast, in the DCN–IN–CHD system, the lowest triplet energy belongs to CHD. This fact is quite important to the explanation of the different dependence of the product ratios on the CHD concentration for these two sensitizers.

(3) Addition of Indene to Cyclopentadiene. The reaction of 1,3-cyclopentadiene (CPD) with IN initiated by irradiation of DCN in benzene is quite similar to that of CHD described above. Three groups of products are obtained that correspond to dimers

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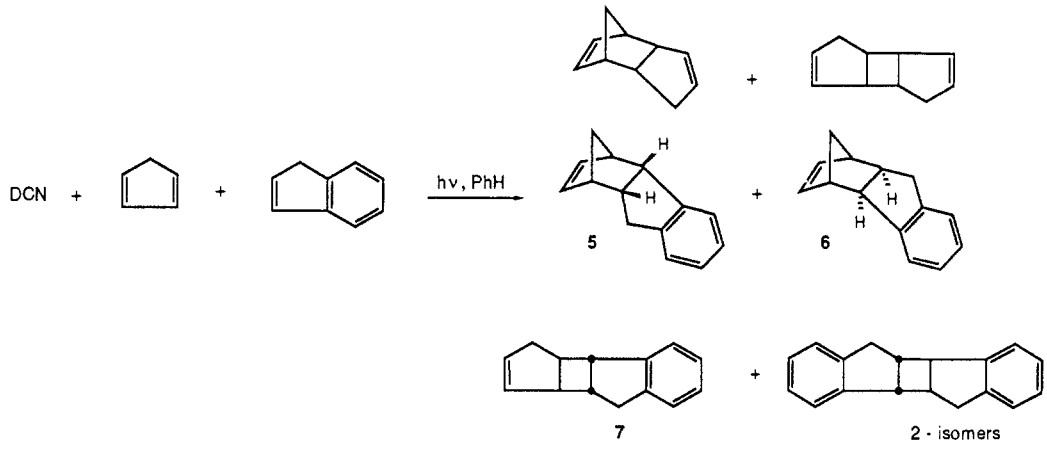
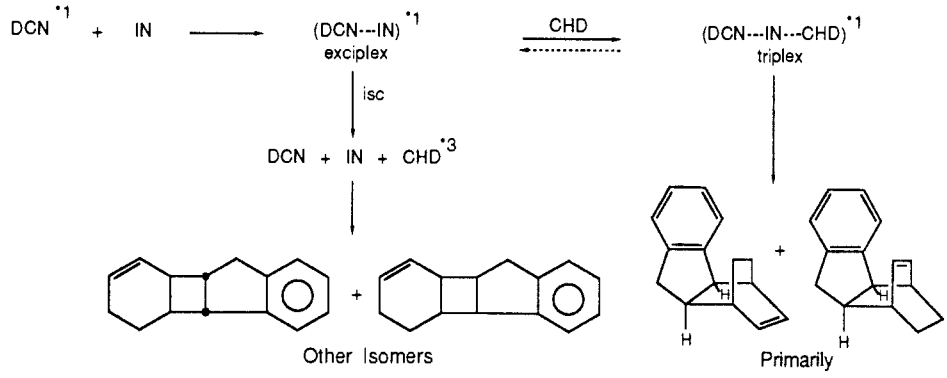
Scheme II



Scheme III



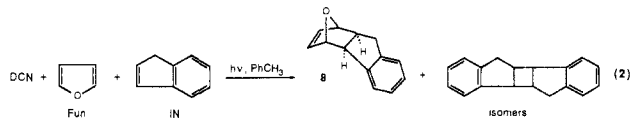
of CPD, adducts of IN to CPD, and IN dimers (Scheme II). These products were identified by comparison with authentic samples independently prepared.[25]

The adducts of IN and CPD consist of three isomeric compounds, a [2 + 2] adduct (**7**), and two [4 + 2] adducts (**5** and **6**). The composition of this mixture depends on the starting concentrations of IN and CPD. When these are 0.86 and 0.48 M, respectively, the ratio of [2 + 2] to [4 + 2] addition is 1:11 and the ratio of *endo*-**5** to *exo*-**6** is 1:1.4.

For comparison, triplet sensitization of the IN, CPD mixture gives products **5**, **6**, and **7** in a ratio of 1:3:4.5, i.e., a much higher proportion of the [2 + 2] adduct. The thermal Diels–Alder reaction of IN and CPD was investigated by Alder and Rickert.[25] We find, as did the earlier workers, that it yields a mixture of [4 + 2] adducts **5** and **6** in a ratio of 4.7:1. Thus, in comparison, the DCN initiated process forms [4 + 2] adducts much richer in the exo isomer than does the thermal reaction.

The IN–DCN exciplex is quenched by CPD. Although we did not study this reaction in detail, qualitatively CPD behaves just like CHD.

(4) Addition of Indene to Furan. Irradiation of DCN in a toluene solution containing IN and furan (FUN) at 0 °C (cold because of the volatility of the FUN) gives dimers of IN and a single adduct of IN to FUN (eq 2). The adduct is identified as the exo-[4 + 2] isomer (**8**) on the basis of its ^{1}H NMR spectrum (see the Experimental Section).[8]



Adducts of IN to FUN are not formed in the triplet-sensitized reaction with isopropylthioxanthone; only IN dimers are found. Similarly, the thermal reaction at 190 °C does not give any of the Diels–Alder product.

The fluorescence of the DCN–IN exciplex is quenched by FUN. This reaction is much slower than the analogous process for CHD. Measurement of the quenching rate constant by analysis of the exciplex lifetime at increasing FUN concentration yields a value of 3.7×10^6 M^{-1} s^{-1}, some two orders of magnitude less than for CHD.

(5) Attempted Addition of Indene to Other Dienes. The DCN initiated addition of IN to 2,5-dimethylfuran, *N*-methylpyrrole, and thiophene was attempted. None of these cyclic dienes give a detectable yield of [4 + 2] adduct. The first two quench the DCN–IN exciplex rapidly, but thiophene does not.

Discussion

The most significant finding of this work is a route for the acceleration of some normally sluggish Diels–Alder reactions of relatively electron-rich components. This result has potential synthetic and mechanistic importance. Our findings do not lead inexorably to a firm, unique mechanistic conclusion. However, certain broad features of the "Triplex-Diels–Alder" reaction are clear. The mechanistic hypothesis we currently favor, illustrated for IN and CHD, is shown in Scheme III.

The excited singlet state of DCN is a potent one-electron acceptor.[30] When it combines with an electron donor in a nonpolar solvent the complex that results has a high degree of charge transfer from the donor to DCN. Under the conditions used in the triplex-Diels–Alder reaction there are two possible donors whenever the cycloaddition is not a simple dimerization. In the illustrated example, the two-component complex that is on the path to Diels–Alder cycloaddition is identified as the DCN–IN exciplex rather than the complex formed from DCN and CHD. Although it is not possible to be absolutely certain about this assignment, there are several experimental and theoretical factors that support it. We will return to this point below.

The DCN–IN exciplex clearly has several reaction paths available to it. Two of these are shown on Scheme III. First, intersystem crossing of the exciplex to a triplet complex will generate eventually the local triplet state of the component with lowest energy (CHD in this case). Second, the exciplex can be captured by a second donor (CHD) to form a ternay complex (DCN–IN–CHD, the triplex) that is suggested to be the precursor

of the Diels–Alder adducts. In addition to these two reactions, the exciplex is probably consumed by irreversible addition of DCN to the donor, as has been observed for anthracene derivatives,[21,26] and by capture of a second molecule of IN to form a DCN–IN–IN triplex (the lifetime of the exciplex decreases as the IN concentration increases). This latter species is suspected as a precursor to a portion of the dimeric IN products we observe.

A major source of support for the mechanism described above is the dependence of the product mixture on the concentration of IN and CHD. In particular, the data shown in Figure 1 reveal that the composition of the IN to CHD adducts changes from that typical of the triplet sensitized reaction to one much richer in [4 + 2] addition products as the concentration of CHD is raised from 0.05 to 1.7 M. An important fact about this experiment is that even at the lower CHD concentrations nearly all of the DCN^{*1} is captured by IN before it intersystem crosses or is consumed in some other way. Since formation of this exciplex is irreversible, and since CHD has been shown to quench the exciplex rapidly, it seems reasonable to associate this quenching process with the [4 + 2] cycloaddition reaction. In this model, the "unquenched" exciplex leads eventually to triplet CHD and to a product mixture richer in its [2 + 2] adducts with itself and with IN. Consistent with this picture is the observation that when DCA replaces DCN as the sensitizer, triplet [2 + 2] adducts of CHD never make a major contribution to the product mixture. In contrast to DCN, DCA has a lower triplet energy than both IN and CHD. Thus, intersystem crossing of either the DCA–IN or DCA–CHD (vide infra) exciplex should give eventually DCA^{*3} which cannot initiate the triplet cycloaddition reactions.

Capture of the DCN–IN exciplex by CHD must involve a ternary complex. These triplexes were first observed by Beens and Weller,[28] and all experimental and computational studies to date show that they adopt the unsymmetrical (acceptor–donor–donor) structure.[29] This order follows logically from the observation that the exciplex is strongly polarized with the donor at the electron-deficient end. Our observations require a ternary complex on the reaction coordinate, but they do not indicate whether this species is a true intermediate or merely the transition state in the cycloaddition.

The mechanism suggested in Scheme III is formulated with the triplex DCN–IN–CHD as the precursor to the Diels–Alder adducts. The data do not require this. The findings can also be understood with the postulation of a triplex having the diene rather than the dienophile as its central component, i.e., DCN–CHD–IN. A triplex with this structure could presumably arise by the capture of an undetected exciplex formed from DCN^{*1} and CHD by IN. Although this alternative formulation cannot be excluded by our kinetic observations (formation of either triplex is first order in the two donor components), it seems less likely. At high IN concentration, the yield of CHD–IN adducts initially increases with CHD concentration, reaches a maximum at ca. 0.3 M, and then decreases. At low relative IN concentration, the fraction of [4 + 2] CHD–IN addition product increases monotonically with the CHD concentration. The first observation is equally consistent with either triplex formulation, but the latter favors our proposal since the DCN–CHD exciplex can only give the mixed addition product if it is captured by IN. However, this argument is not entirely conclusive since increasing the CHD concentration could be inhibiting CHD^{*3} formation by capturing an unobserved DCN–CHD exciplex.

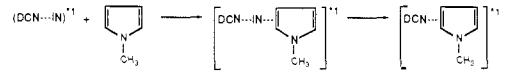
It is well-known that Lewis acids will catalyze some normally sluggish Diels–Alder reactions.[2] The usual explanation for this observation is that complex formation between the dienophile and the electron-withdrawing Lewis acid lowers the barrier to reaction.[31] There appears to be a close parallel between Lewis acid catalysis and the triplex reaction we have investigated. In this scenario, the exciplex plays the role of the Lewis acid–dienophile complex. The spectral measurements indicate a high degree of charge transfer from IN to DCN in this exciplex. Thus, IN is converted from a rather electron-rich dienophile to one that is decidedly electron-poor by complexation with DCN^{*1}. In effect, this is conceptually identical with conventional Lewis acid catalysis except that the exciplex is created in situ by activation with light. To the extent that the Lewis acid model is correct, it supports the formulation DCN–IN–CHD for the structure of the reactive triplex.

Table II. Stern–Volmer Slopes and Fluorescence Quenching Constants for DCN in Benzene

compound	$k_q\tau$, M^{-1}	k_q, M^{-1}
1,3-cyclohexadiene	86.1 ± 0.1	7.0 ± 10^9
indene	82.8 ± 0.4	6.7×10^9
furan (in toluene)	8.8 ± 0.1	7.2×10^8
thiophene	19 ± 0.3	1.5×10^9
1-methylpyrrole	144 ± 0.5	1.2×10^{10}

An important feature of the normal Diels–Alder reaction is its usually predictable stereochemical outcome. In this connection, the thermal addition of IN to the cyclic dienes employed in this study gives product mixtures that are endo-rich (no adduct could be obtained from furan). In contrast, the triplex-Diels–Alder reaction yields mixtures that contain a much higher proportion of the exo isomer (the exo isomer is actually the predominant product in the reaction of CPD). We suggest that this effect arises from steric destabilization of the more crowded endo transition state in the triplex sandwich structure. We should note that in the usual Lewis acid catalyzed reaction, endo selectivity is actually increased beyond that seen in the uncatalyzed process. This fact is typically attributed to an increase in the magnitude of the secondary orbital interaction that causes the endo selection in the first place.[32] A tight triplex sandwich would be much more susceptible to steric effects than the usual Lewis acid transition state that has the electron-withdrawing acid dangling from some appended heteroatom.

Finally, some information can be gleaned from consideration of the dienes that fail to undergo the triplex-Diels–Alder reaction with IN. Thiophene does not quench the fluorescence of the DCN–IN exciplex. This probably is a consequence of its high oxidation potential (1.9 V vs. SCE).[33] On the other hand, 2,5-dimethylfuran and *N*-methylpyrrole both quench the exciplex very rapidly. They have oxidation potentials that are quite low, 1.20 and 1.25 V, respectively.[34] As a consequence, the DCN–*N*-methylpyrrole exciplex, for example, will be considerably lower in energy than the DCN–IN exciplex (the oxidation potential of IN is 1.70 V). Thus, exciplex substitution, eq 3, in these cases may overcome the cycloaddition of the triplex.[29] This points to a possible restriction to the generality of the triplex-Diels–Alder reaction. Only when the diene and the dienophile components have similar oxidation potentials does [4 + 2] cycloaddition appear to occur with measurable efficiency. We are continuing to investigate this and other aspects of the triplex-Diels–Alder reaction.



(3)

Experimental Section

Materials. Benzene and toluene were shaken with cold, concentrated H_2SO_4 until the acid layer was not discolored. Benzene was distilled from sodium and toluene from CaH_2. 1,3-Cyclohexadiene (Aldrich 96%) was distilled fractionally from $NaBH_4$. Indene (Aldrich Gold Label, 99+%)

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was filtered through a plug of silica gel and was distilled fractionally under vacuum (20 Torr, bp 68 °C). Dicyclopentadiene (Aldrich 95%) was cracked at 200 °C. A fraction boiling at 38 °C was taken and used immediately. Furan (Eastman Kodak, 90%) and 2,5-dimethylfuran (Aldrich 99%) were shaken with 5% aqueous KOH until the aqueous layer was no longer discolored. The compounds then were distilled under N_2. Thiophene (Aldrich Gold Label, 99+%) was dried over KOH and then distilled under N_2. 1-Methylpyrrole (Aldrich 99%) was dried over $CaSO_4$ and distilled from KOH. 1,4-Dicyanonaphthalene was prepared as previously described.[35] 9,10-Dicyanoanthracene (Eastman Kodak, 98%) was used without further purification. The actinometer was obtained from Aberchromics Ltd.[36]

Fluorescence Quenching of DCN. Stern–Volmer analyses of the relative intensity of the DCN fluorescence ($\lambda_{excitation}$ = 340 nm, $\lambda_{emission}$ = 382 nm) by alkenes gave straight lines (Table II). The lifetime of DCN in benzene was determined to be 12.4 ns.

DCN-Sensitized Reaction of IN and CHD. Irradiation of a benzene solution of DCN, IN, and CHD (0.42 M) gives three sets of products. One is the CHD dimers[12] and another is the IN dimers.[37,38] The third set of products is composed of 1:1 adducts of CHD and IN. This third set was resolved into four product peaks by capillary gas chromatography, which were analyzed by GC/MS on a packed column; the four adducts could be resolved into two peaks, each containing two isomers. NMR spectra were obtained from samples collected by preparative gas chromtography. Peaks 1 and 2: GC/MS (EI), *m/s* (rel intensity) 196 (10), 117 (15), 116 (100), 115 (20), 80 (35), 79 (12). Exact mass calcd for $C_{15}H_{16}$: 196.12515. Found: 196.12805. ^{1}H NMR ($CDCl_3$) δ 7.37–6.96 (m, 4 H), 6.42 (m, 0.6 H), 6.06 (m, 0.7 H), 5.94 (m, 0.7 H), 3.40–3.04 (m, 2 H), 2.89–2.40 (m, 4 H), 1.75–1.10 (m, 4 H). The two isomers were present in a 2.4:1 ratio as evidenced by capillary gas chromatography. They were identified as the endo (δ 6.06, 5.94) and exo (δ 6.42) [4 + 2] adducts by NMR and by comparison to independently synthesized material.[25] Models of the isomers revealed that the vinyl hydrogens of the endo isomer are in the shielding region of the aromatic ring and are in quite different chemical environments. On the other hand, the vinyl hydrogens of the exo isomer are not affected by the aromatic ring and are in similar chemical environments.

The other products were identified as [2 + 2] adducts by the same methods. GC/MS (EI), peak 3, *m/z* (rel intensity) 196 (13), 178 (10), 165 (15), 152 (12), 141 (12), 117 (30), 116 (100), 115 (50), 80 (70), 79 (25). Exact mass calcd for $C_{15}H_{16}$: 196.12515. Found: 196.12701. GC/MS (EI), peak 4, *m/z* (rel intensity) 116 (100), 115 (20), 80 (30), 79 (12). Exact mass calcd for $C_{15}H_{16}$: 196.12515. Found: 196.12848. Peaks 3 and 4: NMR ($CDCl_3$) δ 7.33–7.07 (m, 4 H), 6.05 (0.74 H), 5.9 (m, 0.74 H), 5.64 (m, 0.52 H), 3.98 (m, 0.26 H), 3.40–2.57 (m, 3.74 H), 2.37–2.09 (m, 2 H), 1.72–1.25 (m, 2 H). Capillary gas chromatography shows a 2.8:1 ratio for peak 3 to peak 4. A similar argument to that put forth above was used to assign the structures. The vinyl hydrogens of the anti-[2 + 2] adduct are not perturbed by the aromatic ring and the syn-[2 + 2] vinyl hydrogens are.

DCN-Sensitized Reaction of IN and CPD. Three 1:1 adducts of CPD and IN were obtained from the irradiation of a benzene solution containing DCN, IN, and CPD (0.25 M) along with CPD dimers and IN dimers.[37,38] The three peaks were observed in a 4.6:6.3:1 ratio. GC/MS (EI), peak 1, *m/z* (rel intensity) 182 (0.9), 117 (10), 116 (100), 115 (20), 66 (5), 39 (10). GC/MS (EI), peak 2, *m/z* (rel intensity) 182 (1.7), 117 (8), 116 (100), 115 (20), 66 (3), 39 (5). GC/MS (EI), peak 3, *m/z* (rel intensity) 117 (10), 116 (100), 115 (20), 66 (4), 39 (8). These samples were identified as the endo-[4 + 2], exo-[4 + 2], and [2 + 2] adducts of CPD and IN, respectively, by comparison with authentic samples.[25]

DCN-Sensitized Addition of IN to FUN. A single 1:1 adduct was isolated by spinning disk chromatography after irradiation of a toluene solution of DCN, IN, and FUN (0.55 M) at 0 °C. A crude white solid was obtained: mp 50–51 °C; GC/MS (EI), *m/z* (rel intensity) 184 (5), 165 (25), 155 (30), 153 (52), 152 (63), 151 (25), 141 (20), 139 (20), 128 (99), 116 (100). ^{1}H NMR ($CDCl_3$) δ 7.36–7.12 (m, 4 H), 6.48 (dd, 1 H, J_1 = 5.5 Hz, J_2 = 1.6 Hz), 6.40 (dd, 1 H, J_1 = 5.5 Hz, J_2 = 1.6 Hz), 4.84 (d, 1 H, J = 1.3 Hz), 4.81 (d, 1 H, J = 1.3 Hz), 3.37 (d, 1 H, J = 6.9 Hz), 3.11 (dd, 1 H, J_1 = 17.7 Hz, J_2 = 9.9 Hz), 2.85 (dd, 1 H, J_1 = 16.8 Hz, J_2 = 3.3 Hz), 2.62 (m, 1 H). ^{13}C NMR ^{1}H-decoupled ($CDCl_3$) δ 145.7, 143.0, 136.5, 136.3, 127.1, 126.4, 124.7, 124.0, 85.1, 84.0, 52.9, 42.1, 35.9. The adduct was determined to be the exo isomer on the basis of the coupling constants for the bridgehead hydrogens. Models predict that the coupling constant between the bridgehead hydrogens and the hydrogens on the neighboring saturated carbon will be less than 1 Hz for the exo isomer and about 5 Hz for the endo isomer.

Preparative Scale Irradiation of DCA, IN, and CHD. A 50-mL deoxygenated benzene solution containing DCA, IN (4.8 g), and CHD (840 mg) was irradiated with a 450-W Hg lamp through a uranium filter in a doughnut-shaped vessel cooled by a water jacket and forced air. DCA was added periodically to maintain a saturated solution (total 250 mg). The Diels–Alder products were isolated by spinning disk chromatography and characterized by their NMR spectra (vide supra). The adducts of IN and CHD were obtained in 37.3% yield; 85% of the mixture was [4 + 2] adducts (endo:exo = 2.4:1) and 15% was [2 + 2] products (anti:syn = 4.1:1).

Acknowledgment. We thank specially Professor Faulkner of this Department for the loan of single-photon-counting and cyclic voltammetric equipment. This work was supported by a grant from the National Science Foundation.

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