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TRIPLEX CATALYZED DIELS-ALDER REACTIONS: ADDITION OF INDENE TO 1,3-CYCLOHEXADIENE

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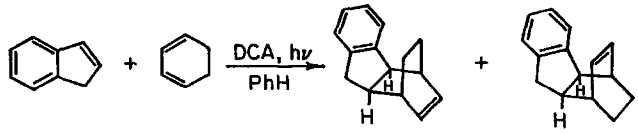
Abstract. The [4+2] cycloaddition (Diels-Alder reaction) of 1,3-cyclohexadiene (**CHD**) to indene (**In**) is catalyzed by the singlet excited state of cyanoarenes such as 1,4-dicyanonaphthalene (**DCN**) and 9,10-dicyanoanthracene (**DCA**).

The Diels-Alder reaction ranks with the most versatile methods for formation of carbon-carbon bonds.[1] It is well known that this reaction proceeds readily under mild conditions when the diene and dienophile carry substituents with strong, opposite electronic bias. However, the reaction of electronically unaffected partners usually requires forcing conditions. Herein we describe a procedure that accelerates a normally sluggish Diels-Alder reaction. This is illustrated with the addition of indene (**In**) to 1,3-cyclohexadiene (**CHD**) to give [4+2] adducts **1** and 2 in good yield, Eq. 1.



(1)

In CHD 1(Exo) 2(Endo)

Irradiation of a benzene solution containing a catalytic amount of 9,10-dicyanoanthracene (**DCA**), **In**, and **CHD** at room temperature gives three groups of products in a mole ratio of 1:4:13.[2] The first group consists of **In** dimers,[3,4] the second is a mixture of **CHD** dimers,[5] and the third contains adducts of **CHD** to **In.**[6] The **In-CHD** adduct group contains 85% [4+2] addition product as a mixture of exo isomer **1** and endo isomer **2** (1:2.4), and 1% [2+2] addition products. In a typical run, a 50 mL solution containing 4.8 g of **In**, 840 mg of **CHD**, and 250 mg of DCA was irradiated through a uranium glass filter with a 450 W Hanovia mercury lamp for 10 h at room temperature. Separation of the reaction mixture by silica gel chromatography gives 620 mg of Diels-Alder adducts **1** and **2**. Similar results are obtained when 1,4-dicyanonaphthalene (**DCN**) is the sensitizer except that more **CHD** dimers are formed.[7] For comparison, the thermal Diels-Alder reaction of **In** and **CHD** requires 24 h at 200°C and gives adducts **1** and **2** in a ratio of 15:1.[8]

The fluorescence of **DCN** in benzene is quenched at a diffusion limited rate by **In** ($k_q\tau$ = 83 $\underline{M}^{-1}$). This process creates an exciplex that is readily detected by its characteristic emission (λ_{max} = 458 nm, τ (0.017 $\underline{M}$ **In**) = 48 ns). The **In-DCN** exciplex in turn is quenched by **CHD** ($k_q = 3.5 \times 10^8\ \underline{M}^{-1}\ s^{-1}$). We suggest that reaction of the **DCN-In** exciplex with **CHD** forms a triplex with structure $(\mathbf{DCN\text{-}In\text{-}CHD})^{*1}$ and that this triplex is the source of Diels-Alder adducts **1** and **2**. A partial mechanism outlining this proposal is shown in Scheme I.[9]

Scheme I

$$\mathrm{DCN} \xrightarrow{h\nu} \mathrm{DCN}^{*1} \qquad (2)$$

$$\mathrm{DCN}^{*1} + \mathrm{In} \longrightarrow \underset{\text{Exciplex}}{(\mathrm{DCN}\text{---}\mathrm{In})^{*1}} \qquad (3)$$

$$(\mathrm{DCN}\text{---}\mathrm{In})^{*1} \longrightarrow \text{Addition; Relaxation; Triplet} \qquad (4)$$

$$(\mathrm{DCN}\text{---}\mathrm{In})^{*1} + \mathrm{CHD} \rightleftharpoons \underset{\text{Triplex}}{(\mathrm{DCN}\text{---}\mathrm{In}\text{---}\mathrm{CHD})^{*1}} \qquad (5)$$

$$(\mathrm{DCN}\text{---}\mathrm{In}\text{---}\mathrm{CHD})^{*1} \longrightarrow \text{Diels-Alder; Relaxation; Triplet} \qquad (6)$$

The exciplex formed from **In** (E_{ox} = 1.45 V vs. Ag/Ag$^+$; irreversible) and **DCN** (E^*_{red} = 2.06 V vs. Ag/Ag$^+$; calculated) is of the sort that is bound together primarily by charge transfer.[11] Measurement of the solvent polarity dependence of the exciplex emission[12] reveals a dipole moment equal to ca. 10 D which corresponds to ca. 40% electron transfer from **In** to **DCN**. Thus, exciplex formation converts **In**, a typical mildly electron rich dienophile, to one that is quite electron poor. Similar electron withdrawal is believed to accelerate Lewis acid catalyzed Diels-Alder reactions.[13]

Triplexes were discovered by Beens and Weller[15] and all experimental[16] and computational studies[17] to date show that they adopt an unsymmetrical (Acceptor--Donor--Donor) structure. Jones[18] suggested that triplexes play a role in the dimerization of **CHD**, a notion we recently confirmed.[10] The present case is the first instance of such a reaction that is not a simple dimerization.

The Diels-Alder reaction of the triplex (Eq. 6) may be closely related to the diene radical cation cyclizations discovered by Freeman[19] and by Hammond[20] and used by Mizuno to add **In** to furans.[21,22] The triplex route, however, is insensitive to oxygen and does not suffer from the side reactions typical of other free radical ion processes. We are continuing to explore the scope and the mechanism of the triplex-catalyzed process.

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2) The ratio of products is dependent on both [**CHD**] and [**In**]. In this example, [**CHD**] = 0.21 and [**In**] = 0.86 M.

3) **In** dimers were identified by GC/MS and by comparison of their proton NMR spectra with those of **In** dimers prepared by triplet sensitization: G. O. Shenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, C. H. Krauch, Chem. Ber. **95**, 1642 (1962).

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6) Four isomeric **In-CHD** adducts were characterized by high resolution GC/MS and by proton NMR spectroscopy.[8]

7) The triplet energy of **DCA** is less than that of **In** or **CHD** while that of **DCN** is above **CHD.** Rapid energy transfer to form **DCA**^{*3} probably quenches the dimerization of triplet **CHD.**

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9) **DCN*** is also quenched by **CHD.** This reaction leads to **CHD** dimers[10] and could be important also in the addition of **In** to **CHD.**

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