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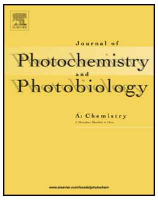

Selective photoisomerization of methyl substituted nitro diphenylbutadienes

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ABSTRACT

A series of *p*-nitro substituted *trans*-diphenylbutadienes is synthesized and their photophysical and photochemical properties are investigated. All the dienes have a very low quantum yield of fluorescence but exhibit remarkable solvatochromic emission shifts attributed to twisted intramolecular charge transfer. Photochemical irradiation of simple *p*-nitro substituted diphenylbutadienes reveals inefficient or no detectable photoisomerization. However, substituting a methyl group on the butadiene chain of *p*-nitro substituted diphenylbutadiene or replacing the nitro group with cyano group yields the corresponding *trans*–*cis* isomers. In the case of simple nitrodienes, strong intramolecular charge transfer character in the excited state aids dissipation of absorbed energy through non-photochemical and non-radiative channels. The steric effect caused by the presence of methyl group lowers the isomerization barrier in methyl substituted dienes leading to a regioselective isomerization.

1. Introduction

Light induced isomerization around a double bond is an important step for many biologically important pigments such as the opsin family of proteins [1,2]. To understand this highly rapid and efficient *trans*–*cis* photoisomerization of all-*trans* retinal to 13-*cis* retinal in bacteriorhodopsin [3] and 11-*cis* to all-*trans* retinal in rhodopsin [2], diphenylpolyenes have been extensively investigated as model compounds. Their utility as model compounds arose in part because of their energy level proximity with retinyl polyenes and visual pigments [4]. Apart from the photochemical processes, the emission and photoswitchable properties of such arylethylene derivatives in solution and solid state have also found utility in a variety of biological [5–9] and materials applications [10–12]. Photoisomerization of 1,4-diphenylbutadiene leads to the formation of the corresponding *cis*–*trans* isomers and *trans*–*cis* isomers and isomerization is presumed to happen *via* perpendicular intermediates [13]. Rigorous mechanistic investigations of photoisomerization of diphenylbutadiene and other polyenes revealed involvement of Bicycle Pedal (BP) and Hula twist (HT) pathways [14–21]. Both BP and HT pathways were utilized to explain the specificity of photoisomerization of the opsin proteins despite the protein imposed volume restrictions [15]. Although detailed photochemical investigations utilizing diphenylbutadiene were communicated, isomerization of substituted diphenylbutadienes [22–24] has received little attention in comparison to their fluorescence spectroscopic investigations [25–31]. In specific, diphenylbutadienes substituted with donor or acceptor groups yields one-photon-one bond isomerization of the C=C bond lying closer to the acceptor group [23,32]. Similarly photoisomerization of *trans,trans,trans* *p*-methoxy-*p*′-nitro substituted diphenylhexatriene derivative yielded a regioselective *cis* isomer [33]. Recent investigations on similar butadiene containing systems reveal significant influence of the methyl group or halogen group on the photoinduced behavior [34,35] and efficient *trans* to *cis* isomerization of dendrimeric diphenylbutadiene derivatives [36,37]. In general, the observations reveal discrete one-bond rotations, barrier to the isomerization and involvement of competing internal conversion processes [13]. In the current work, we seek to examine the effect of methyl substituent and the nature of substituent on the photoisomerization of a series of diphenylbutadiene derivatives (Fig. 1) in acetonitrile at room temperature. Our results show that substituting methyl group on the double bond and replacing nitro group with a cyano group has a significant influence on the photoisomerization of the diphenylbutadienes examined.

2. Experimental

The reagents required for the synthesis of diphenylbutadiene derivatives were obtained from Sigma-Aldrich, Alfa Aeser, Akcros

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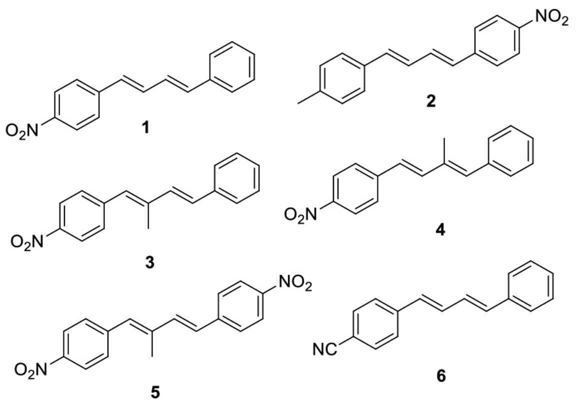


Fig. 1. Structures of diphenylbutadienes investigated.

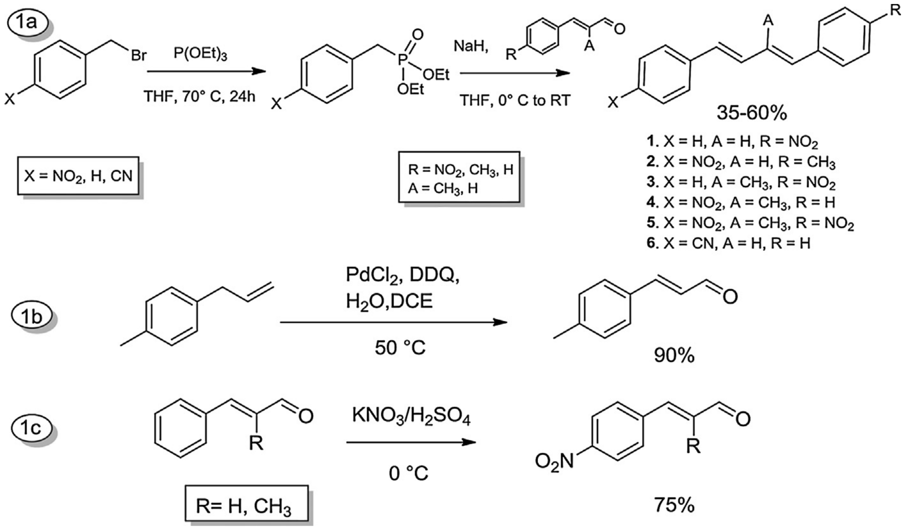
and S.D. Fine Chemicals India. The solvents needed for the synthesis and spectral studies were dried using reported procedures. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ with tetramethylsilane as internal standard using a 500 MHz Bruker Avance spectrometer. Absorption spectra were recorded on Analytikjena, Specord 210 model UV–vis spectrophotometer. HPLC was done using Agilent 1260 infinity fitted with Kinetex 5 μm C18 100 Å (250 × 4.6 mm) column. 65% acetonitrile-water eluent conditions at a rate of 1.0 mL/min are used for all the samples. The monitoring wavelengths for detecting the photoproducts are 360 nm and 390 nm. Fluorescence studies were performed using fluorolog-3 spectrofluorimeter and fluorescence quantum yields were calculated using quinine sulfate as a standard [38]. For photochemical irradiation experiments, a sample (3 mL of $\sim 10^{-5}$ M) in acetonitrile was taken in a 1 cm path length quartz cuvette and irradiated using 125 W medium pressure Hg vapor lamp. 10% copper sulphate pentahydrate solution having 100% transmittance from 330 to 560 nm was used as the cut-off solution filter. Progress of the photoisomerization was monitored using UV–vis. spectroscopy. For characterization purposes, a higher concentration of sample solutions (3 mg in 1 mL of $CDCl_3$) was irradiated for 12–16 h using 125 W medium pressure Hg lamp. Quantum yields of photoisomerization (ϕ_{PI}) were performed using potassium ferrioxalate actinometry [39].

2.1. Synthesis

Diphenylbutadiene derivatives utilized in this investigation were prepared by using Horner–Wadsworth–Emmons reaction [23] (Scheme 1a) in about 35–60% yields. In a typical procedure, triethyl phosphite (5.74 mmol) was added to the THF solution of benzyl bromide (2.3 mmol) and refluxed for 24 h under a N_2 atmosphere. The reaction mixture was cooled to room temperature and further cooled to 0 °C using an ice bath. Sodium hydride (11.5 mmol) was added to this mixture and stirred for 5 min. Aldehyde (2.3 mmol) was subsequently added drop wise to the pale/dark pink colored solution and stirring was continued for additional 30 min. In the case of methyl substituted aldehydes, corresponding (*E*) geometric isomer of α-methyl cinnamaldehyde (Aldrich) was used. Thin Layer Chromatography (TLC) was utilized to monitor the progress of the reaction and the reaction was quenched by adding water. The organic layer was extracted using dichloromethane and concentrated under reduced pressure. The crude reaction mixture so obtained was purified by column chromatography using silica gel, 5% ethyl acetate in petroleum ether. Starting materials, 4-methylcinnamaldehyde required for the synthesis of (**2**) and nitro cinnamaldehyde required for synthesis of (**3**) and (**5**), were obtained by DDQ oxidation of 4-allyl toluene [40] (Scheme 1b) and by simple nitration using a nitrating mixture generated by mixing KNO_3 with H_2SO_4 of α-methyl-cinnamaldehyde (scheme 1c), respectively. Characterization data for all the synthesized dienes were given in the Supplementary information.

3. Results and discussion

A series of diphenylbutadiene derivatives containing nitro and cyano substituents are synthesized and examined for their photochemical isomerization behavior. The synthesized dienes (**1**–**6**) are listed in Fig. 1. Diene (**1**) has a *p*-substituted nitro group on the aromatic ring. Diene (**2**) is a *p,p′* disubstituted diphenylbutadiene containing methyl and nitro groups *para* to each other. Dienes (**3**)–(**5**) have a methyl substitution on the double bond. In Diene (**3**), a methyl group is proximal to the aromatic nitro group and in (**4**) the methyl group is placed distal to the nitro group. Diene (**5**) is the same as (**3**) but have nitro groups on both sides of the double bond in the aromatic ring. Through this arrangement,



Scheme 1. (a) Typical synthetic schemes for the synthesis of substituted diphenylbutadienes. (b) Synthesis of 4-methylcinnamaldehyde [40] and (c) nitration of aromatic cinnamaldehydes.