

PHOTOCHEMICAL REACTIONS OF PHENYL-DIENYL NON-CONJUGATED BICHROMOPHORIC SYSTEMS

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Summary

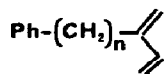
Diverse photochemical behaviour is observed for phenyl-dienyl and phenyl-furanyl non-conjugated bichromophoric systems. Only 2-(2-phenylethyl)buta-1,3-diene and 2-(3-phenylpropyl)buta-1,3-diene yield intramolecular cycloadducts, but the products from neither reflect the expected *para*-1,4 attack.

1. Introduction

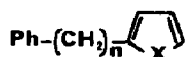
The photochemistry of arene-1,3-diene systems is complex and frequently leads to multicomponent mixtures of products [1] unless either the diene is conformationally fixed [2] or iodine is present as a moderator [3]. The studies of Morrison and coworkers [4] with *cis*- and *trans*-6-phenylhex-2-ene and our own with various phenyl-vinyl systems [5] have shown that the photoreactions of the bichromophores may be directed by conformational and steric effects, and Wender and coworkers [6] have made elegant use of these features for synthetic applications of the intramolecular photocyclization. Intramolecular cycloaddition of phenyl-dienyl compounds offers other synthetic possibilities, and the present investigation was carried out to assess whether the type of control observed in the photoreactions of the monoethenes would operate with conjugated dienes and similarly promote pathway selectivity. Irradiation of such dienyl systems has not previously been reported although anthryl compounds analogous to 3 are known to yield 9,10-2',5' intramolecular cycloadducts [7].

2. Results and discussion

The bichromophores 1, 2 and 3

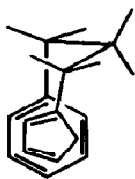


1a, $n = 2$
1b, $n = 3$



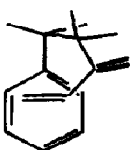
2a, X = CH₂, $n = 2$; 2b, X = CH₂, $n = 3$
3a, X = O, $n = 2$; 3b, X = O, $n = 3$

were chosen to investigate the excited state interactions and reactions between phenyl and dienyl chromophores. Space-filling molecular models indicate that the two chromophores in 1b, 2b and 3b (*i.e.* $n = 3$) can readily interact in a parallel orientation (*e.g.* orientation 4



4

for 2b) with no eclipsing in the intervening $-(CH_2)_3-$ chain, in a manner suggested by Hirayama [8] to account for the fluorescence emission properties of 1,3-diphenylpropane. For 1b such interaction may be expected to be greater for the *cisoid* than for the *transoid* diene conformation since the latter causes some steric clash between the hydrogen atoms at the 1 position on the diene and the hydrogen atoms at the 4 position in the C_3 chain. For these systems it thus appears that the chromophores are ideally aligned for *para*-1,4 (2',5'-1,4 for 1b and 1',4'-1,4 for 2b and 3b) intramolecular photocycloaddition of the phenyl and dienyl moieties; this mode is observed as the major reaction in corresponding intermolecular processes [1, 2]. No such parallel overlap between the chromophores of 2a and 3a is, of course, possible, but their photochemistries and fluorescence spectra were examined for comparison with those of 2b and 3b. It is likewise not possible for the phenyl and dienyl moieties of 2-(2-phenylethyl)buta-1,3-diene 1a to interact in a parallel manner, but interestingly models show that a non-eclipsed ethane unit favours the orientation 5



5

in which the diene adopts a non-planar conformation and the 3,4 ethene then lies over the 2,6 phenyl positions.

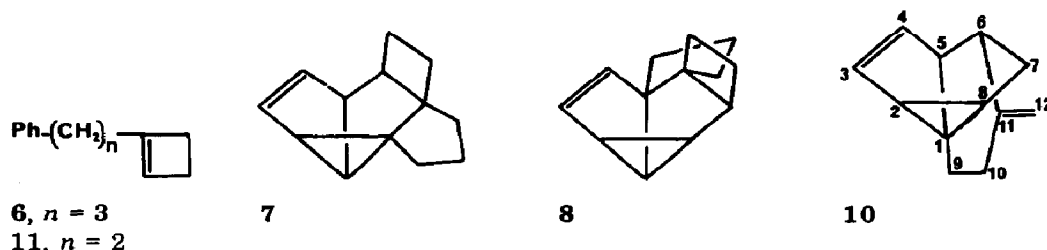
The bichromophores were irradiated (254 nm) as 1% solutions in cyclohexane and the progress of the reactions was monitored by gas-liquid chromatography (GLC) and thin layer chromatography. The photoproducts from 1a and 1b were isolated by preparative GLC and their structures were established from spectroscopic data. The results of the irradiations and the fluorescence emission characteristics of the bichromophores are summarized in Table 1. Degassing under nitrogen had no significant effect on the course of the reaction, but under xenon the yields of photoproducts from 1a and 1b were reduced by approximately 15%. In view of the known effect of

xenon to increase the triplet population of arenes (see for example ref. 9), this result, as in the case of 6-phenylhex-2-yne [10], is taken to imply that the intramolecular cyclization proceeds via the excited singlet state.

TABLE 1

Fluorescence emission characteristics and photochemical products of bichromophores 1 - 3

Bichromophore	Arene fluorescence ^a	Products
1a ^b	Quenched	10 ($\Phi = 0.01$), 11 ($\Phi = 0.001$),
1b	0.001	6 ($\Phi = 0.003$), 7 ($\Phi = 0.005$), 8 ($\Phi = 0.007$) + nine minor products
2a	Quenched	Ill-defined polymeric material
2b	Quenched	Ill-defined polymeric material
3a	0.90	Ill-defined polymeric material
3b	Quenched (weak broad structureless emission centred at 350 nm)	Essentially photostable under reaction conditions

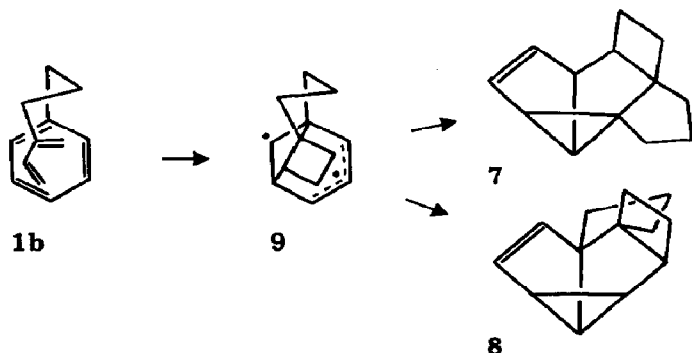


^a Relative to amylobenzene (concentrations, 0.005 M; excitation, 284 nm).

^b Φ of disappearance of 0.025.

It is not understood why neither 2b nor 3b yields the *para*-1,4 cycloadducts as the quenching of the arene fluorescence by the diene indicates efficient excited state interaction between the chromophores. Compound 2b on short irradiation did yield a trace of an isomer, but both this and the starting material were converted into ill-defined polymers in preparative experiments. The furanyl compound 3b shows some evidence for exciplex formation and this may be the energy wastage route which is responsible for its photostability in comparison with 3a. For 1b despite again a seemingly favourable 2',5'-1,4 overlap of the chromophores and efficient interaction between the phenyl and dienyl groups in the excited state, only small amounts of a multicomponent mixture of products which did not include the *para*-1,4 adduct are formed. Surprisingly, however, and in marked contrast with the photochemical reactions of 1a the three major product isomers from 1b do involve both ethene moieties of the diene with the formation of the cyclobutene 6 and the cyclobutene-phenyl *meta* cycloadducts 7 and 8. Although 6 is the obvious precursor of 7 and 8 by 1,3 cycloaddition

of the cyclobutenyl moiety to the phenyl group, the formation of neither of the latter two isomers has an induction period and 6 does not apparently reach a photostationary state. An alternative explanation for the formation of 7 and 8 is that both isomers arise via the intermediate 9 produced by novel 1',3'-2,3 addition of the phenyl and dienyl chromophores:



The conformation of 1b which may result in this addition is very little different from that of the 2',5'-1,4 orientation of the chromophores.

In contrast with the other bichromophoric systems studied, 1a reacts cleanly and, as predicted from molecular models, gives the one intramolecular cycloadduct 10 as the major photoproduct. Thus in this case the bichromophore behaves as a phenyl-ethenyl system with $n = 3$ [4, 5]. The reaction conveniently gives an intramolecular *meta* cycloadduct with functionality on the bridging unit, and with chemical conversions of more than 50% and selectivities of better than 90% the process becomes very attractive for synthetic purposes.

The present results indicate that favourable orientation and efficient interaction in the excited state between chromophores may well be a prerequisite for their intramolecular cycloaddition, but these features do not assure a successful reaction and other, as yet undetermined, energy dissipation routes are more favoured for phenyl-dienyl systems unless the molecular geometry allows a phenyl-ethenyl ($n = 3$) reaction as is observed for 1a but not for 1b.

3. Experimental details

3.1. Synthesis of the bichromophores

3.1.1. 1a and 1b

3-Methyl-2,5-dihydrothiophene 1,1-dioxide (melting point, 64 - 66 °C from ethyl acetate-petroleum ether) was obtained in 48% yield by heating sulphur dioxide and isoprene in methanol at 85 °C in an autoclave. Methyl bromination was achieved by refluxing the sulphone with benzoyl peroxide in chloroform with *N*-bromosuccinimide under illumination from tungsten lamps. Heating the unpurified 3-bromomethyl-2,5-dihydrothiophene 1,1-

dioxide at 170 °C and 20 mmHg produced the bromoisoprene (boiling point, 41 - 42 °C at 20 mmHg) in 39% yield overall. The bromoisoprene in diethyl ether was added dropwise to either benzylmagnesium chloride (1a) or 2-phenethylmagnesium bromide (1b). The bichromophore 1a was purified to better than 99% (boiling point, 63 - 65 °C at 2 mmHg) by conversion to the sulphone, recrystallization from benzene-charcoal (melting point, 84 - 85 °C) and pyrolysis back to 1a at 150 °C and 2 mmHg. 1b was purified (better than 99%) by preparative GLC.

The spectroscopic data for 1a are as follows: δ values (CDCl_3) centred at 7.25 ppm (5 H, multiplet), 6.45 ppm (1 H, doublet of doublets, $J = 17.5$ Hz and $J = 11.0$ Hz), 5.25 ppm (1 H, doublet, $J = 17.5$ Hz), 5.20 - 4.95 ppm (3 H, multiplet) and 3.0 - 2.3 ppm (4 H, overlapped multiplet and doublet of doublets); ν_{max} (liquid smear), 3080, 3060, 3030, 3000, 2980, 2930, 2860, 1805, 1595, 1495, 1455, 900, 895, 745 and 695 cm^{-1} ; M^+ (calculated), 158.1095; M^+ (found), 158.1096.

The spectroscopic data for 1b are as follows: δ values (CDCl_3) centred at 7.18 ppm (5 H, multiplet), 6.36 ppm (1 H, doublet of doublets, $J = 17.0$ Hz and $J = 11.0$ Hz), 5.15 ppm (1 H, doublet, $J = 17.0$ Hz), 5.05 - 4.9 ppm (3 H, multiplet), 2.63 ppm (2 H, triplet, $J = 7$ Hz) and 2.4 - 1.6 ppm (4 H, overlapping multiplets); ν_{max} (liquid smear), 3080, 3060, 3030, 3000, 2980, 2930, 2860, 1595, 1495, 1455, 990, 895, 745 and 695 cm^{-1} ; M^+ (calculated), 172.1250; M^+ (found), 172.1252.

3.1.2. 2a

Cyclopentadiene (0.1 mol) in tetrahydrofuran was added to a slurry of sodium sand (0.11 mol) also in tetrahydrofuran at 10 °C. After the mixture had been heated at 50 °C until reaction ceased, (2-bromoethyl)benzene (0.1 mol) was added over 0.5 h with a maintained temperature of less than 25 °C. The reaction was worked up with aqueous methanol, and 2a was extracted with diethyl ether and distilled at 60 - 63 °C at 0.02 mmHg. The yield was 43%.

The spectroscopic data for 2a are as follows: δ values (CDCl_3) centred at 7.17 ppm (5 H, multiplet), 5.90 - 6.47 ppm (3 H, multiplet) and 2.93 - 2.60 ppm (6 H, multiplets); ν_{max} (liquid smear), 3087, 3065, 3030, 2925, 2859, 1606, 1499, 1455, 1370, 878, 750, 699 and 675 cm^{-1} ; M^+ (calculated), 170.1096; M^+ (found), 170.1098.

3.1.3. 2b

Cyclopentadiene (0.11 mol) in dimethylformamide (DMF) was added over 0.5 h to a sodium hydride-oil dispersion suspended in DMF. (3-Bromopropyl)benzene (0.1 mol) in DMF was added over 0.5 h and the reaction was maintained at less than 25 °C for a further 1 h. The mixture was then poured into water and 2b was extracted with petroleum ether (boiling point, 30 - 40 °C), and the fraction distilling at 64 - 70 °C at 0.015 mmHg was collected. The yield was 36%. 2a and 2b were stored under nitrogen at -78 °C as darkening occurred at room temperature in air.

The spectroscopic data for **2b** are as follows: δ values (CDCl_3) centred at 7.20 ppm (5 H, multiplet), 6.50 - 5.93 ppm (3 H, multiplet), 2.90 ppm (2 H, doublet of doublets), 2.63 ppm (2 H, triplet), 2.60 - 2.23 ppm (2 H, multiplet) and 1.90 ppm (2 H, quartet); ν_{max} (liquid smear), 3090, 3065, 3030, 2935, 2859, 1606, 1500, 1455, 1369, 1078, 1031, 949, 931, 899, 811 and 745 cm^{-1} ; M^+ (calculated), 184.1254; M^+ (found), 184.1252.

3.1.4. *3a*

An equimolar amount of diethylbenzylphosphonate and furfural was added to a suspension of sodium methoxide in tetrahydrofuran. The yellow precipitate of 2-styrylfuran (53%) formed on addition of water was filtered and recrystallized from ethanol. Hydrogenation was carried out at 68 lbf in^{-2} over Adam's catalyst in methanol. Purification of **3a** was achieved by preparative GLC.

The spectroscopic data for **3a** are as follows: δ values (CDCl_3) centred at 7.25 ppm (1 H, multiplet), 7.15 ppm (5 H, multiplet), 6.18 ppm (1 H, doublet of doublets, $J = 2 \text{ Hz}$ and $J = 3 \text{ Hz}$), 5.90 ppm (1 H, broad doublet, $J = 3 \text{ Hz}$) and 2.96 ppm (4 H, multiplet); ν_{max} (liquid smear), 3120, 3090, 3070, 3030, 2920, 2860, 1600, 1505, 1500, 1455, 1150, 1075, 1010, 935, 925, 885, 800, 730 and 695 cm^{-1} ; M^+ (calculated), 172.0888; M^+ (found), 172.0895.

3.1.5. *3b*

Furfural (0.07 mol) was added over 15 min to 2-phenethylmagnesium bromide (0.07 mol) in diethyl ether. After conventional work-up, a 95% yield of the alcohol was obtained. Dehydration of the alcohol was achieved by distillation at 0.004 mmHg up a neutral alumina column with 20 wt.% pyridine. The fraction boiling at 76 - 80 °C at 0.004 mmHg was hydrogenated in methanol at atmospheric pressure using 10% Pd/C. **3b** was isolated in an overall yield of 20%.

The spectroscopic data for **3b** are as follows: δ values (CDCl_3) centred at 7.25 ppm (1 H, multiplet), 7.20 ppm (5 H, multiplet), 6.20 ppm (1 H, doublet of doublets, $J = 2 \text{ Hz}$ and $J = 3 \text{ Hz}$), 5.90 ppm (1 H, broad doublet, $J = 3 \text{ Hz}$), 3.00 - 2.80 ppm (4 H, multiplet) and 1.9 - 1.6 ppm (2 H, multiplet); ν_{max} (liquid smear), 3120, 3090, 3060, 3030, 2940, 2860, 1600, 1505, 1500, 1455, 1150, 1080, 1005, 925, 795, 730 and 695 cm^{-1} ; M^+ (calculated), 186.1045; M^+ (found), 186.1055.

3.2. Isolation of the photoproducts from *1a* and *1b*

The bichromophore **1a** (0.5 g) was irradiated (254 nm) in cyclohexane (50 ml) for 40 h; this produced a 55% conversion of **1a** to **10** and **11** in a 10:1 ratio. (The Carbowax 20M relative retention times for **10**, **1a** and **11** were 0.73, 1.00 and 1.05 respectively.) The photoproducts were isolated by preparative GLC, but **11** always contained about 5% of **1a** by this procedure. The structures of **10** and **11** are based on spectroscopic data particularly those from ^1H nuclear magnetic resonance (NMR) spectroscopy and extensive spin decoupling.

The spectroscopic data for 10 are as follows: δ values (250 MHz; CDCl_3) 0.89 ppm (H(8), $J_{2,8} = 8.5$ Hz, $J_{8,7} = J_{8,7'} = 5$ Hz), 1.68 ppm (H(7), H(7') and H(9), unresolved multiplet), 2.17 ppm (H(9'), unresolved multiplet), 2.29 ppm (H(5), $J_{5,2} = 4$ Hz, $J_{5,4} = 2$ Hz), 2.48 ppm (H(10) and H(10'), unresolved multiplet), 2.60 ppm (H(2), $J_{2,8} = 8.5$ Hz, $J_{2,3} = 4$ Hz, $J_{2,4} = 1.5$ Hz, $J_{2,5} = 4$ Hz), 2.95 ppm (H(6), unresolved broad doublets), 4.68 and 4.72 ppm (H(12) and H(12'), $J_{\text{gem}} = 12.5$ Hz), 5.53 ppm (H(4), $J_{4,2} = 1.5$ Hz, $J_{4,3} = 6$ Hz, $J_{4,5} = 2$ Hz) and 5.74 ppm (H(3), $J_{3,2} = 4$ Hz, $J_{3,4} = 6$ Hz); M^+ (calculated), 158.1095; M^+ (found), 158.1097.

The spectroscopic data for 11 are as follows: δ values (220 MHz; CDCl_3) 1.35 ppm (4 H, multiplet), 2.45 ppm (2 H, multiplet), 2.78 ppm (2 H, triplet, $J = 3$ Hz), 5.74 ppm (1 H, singlet) and 7.26 ppm (5 H, multiplet); M^+ (mass spectrometry (MS)-GLC) = 158 a.m.u.

Irradiation of 1b (0.5 g) in cyclohexane (50 ml) for 10 days with periodic cleaning of polymer deposits produced nine photoisomers ($M^+ = 172$ a.m.u. (MS-GLC)) and traces of three non-isomeric products. The three major isomers (Carbowax relative retention times for 7, 8, 1b and 6 of 0.57, 0.60, 1.00 and 1.05 respectively) were isolated by preparative GLC but, because of the complexity of the mixture and the low concentrations, contamination (about 5%) with other photoisomers was always evident. Structures were assigned principally from ^1H NMR spectral data (220 MHz; CDCl_3).

The spectroscopic data for 7 are as follows: 1.1 - 2.1 ppm (10 H, unresolved multiplets), 2.15 ppm (H(2), doublet of doublets, $J_{2,3} = 2.2$ Hz, $J_{2,1} = 6$ Hz), 2.30 ppm (H(1), triplet, $J_{1,5} = J_{1,2} = 6.5$ Hz), 2.85 ppm (H(6) (*exo*), broad triplet, $J_{6,5} = 5.5$ Hz, $J_{6,x} = 9$ Hz, $J_{6,y} = 2$ Hz), 3.24 ppm (H(5), broad triplet, $J_{5,1} = 6.5$ Hz, $J_{5,6} = 5.5$ Hz, $J_{5,4} = 2.2$ Hz), 5.84 ppm (H(4), doublet of doublets, $J_{4,3} = 5.5$ Hz, $J_{4,5} = 2.2$ Hz) and 5.90 ppm (H(3), doublet of doublets, $J_{3,4} = 5.5$ Hz, $J_{3,2} = 2.2$ Hz).

The spectroscopic data for 8 are as follows: 1.5 - 2.1 ppm (12 H, unresolved multiplets which can be discerned by spin decoupling, H(8), multiplet, and H(2), multiplet, $J_{2,1} = 6.5$ Hz, $J_{2,3} = 2.2$ Hz), 2.52 ppm (H(1), triplet, $J_{1,2} = J_{1,8} = 6.5$ Hz), 3.02 ppm (H(7) (*exo*), triplet of doublets, $J_{7,8} = 9$ Hz, $J_{7,9} = J_{7,9'} = 6.5$ Hz), 5.68 ppm (H(4), doublet, $J_{4,3} = 5.5$ Hz) and 5.82 ppm (H(3), doublet of doublets, $J_{3,4} = 5.5$ Hz, $J_{3,2} = 2.2$ Hz).

The spectroscopic data for 6 are as follows: 1.5 - 2.2 ppm (4 H, overlapping multiplets), 2.2 - 2.5 (4 H, broad singlet), 2.64 ppm (2 H, triplet, $J = 5$ Hz), 5.74 ppm (1 H, singlet) and 7.25 ppm (5 H, multiplet).

Bichromophore 3b was essentially photostable under the above irradiation conditions, but 2a, 2b and 3b produced white insoluble materials which had broad indistinct IR and ^1H NMR spectra and which were judged to be polymeric. Quantum yields were assessed using a merry-go-round apparatus by comparison with the known efficiencies of the intramolecular cycloaddition reactions of 5-phenylpent-1-ene [5]. The irradiated solutions were analysed by GLC following calibration of the instrument for response to the bichromophores and their photoproducts, and *cis* and *trans* decalins were

used as the internal standard. Measurements were taken at less than 5% reactant conversion.

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