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PHOTOCHEMISTRY OF CONJUGATED POLYACETYLENES: PHOTOREACTION OF 1,4-DIPHENYL-1,3-BUTADIYNE WITH DIMETHYL FUMARATE

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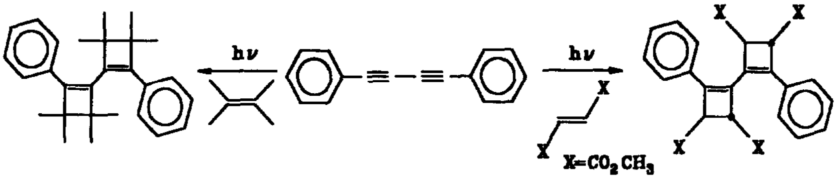
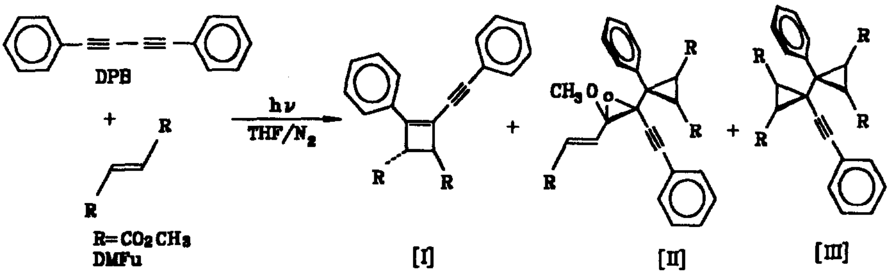
Summary: Irradiation of 1,4-diphenyl-1,3-butadiyne (DPB) with dimethyl fumarate (DMFu) in deaerated tetrahydrofuran yields a primary 1:1 photoadduct I and further irradiation of the solution results in the formation of novel 1:2 photoadducts, II and III as the secondary photoadducts.

The photochemistry of conjugated polyacetylenes has received relatively little attention compared to corresponding olefins. We had previously reported the photoreaction of 1,4-diphenyl-1,3-butadiyne with some olefins such as 2,3-dimethyl-2-butene(DMB) and dimethyl fumarate(DMFu).[1(a)]



We obtained, however, 1:1 cyclobutene and 1:2 cyclopropyl addition products from photoreactions of conjugated polyacetylenes with olefins,[1(b)-(e)] and we have reinvestigated the photoreactions of DPB with the same olefins. Detailed study on the photoreaction of DPB with an electron rich olefin, DMB, has been reported[1(b)] and our previous structural assignment of the products were proven to be incomplete and/or wrong. In this investigation, we report more detailed photocycloaddition reaction of DPB with an electron deficient olefin, DMFu.



Scheme 1

Irradiation of DPB(4mmol) with DMFu(100 mmol) in deaerated THF at 300 nm yields a 1:1 photoadduct, 1-(phenylethynyl)-2-phenyl-*trans*-3,4-bis(methoxycarbonyl)-cyclobutene(I),[2] and 1:2 photoadducts, 2-(*trans*-methoxycarbonyl)ethenyl-2-methoxy-3-(1-phenyl-*trans*-2,3-bis(methoxycarbonyl))cyclopropyl-3-phenylethynyloxirane(II)[3] and *trans*-2,3-bis(methoxycarbonyl)-1-(1-phenyl-2,3-bis(methoxycarbonyl))cyclopropyl-1-phenylethynylcyclopropane(III)[4] in 13%, 12%, and 14% yields, respectively(Scheme 1). Dark red products, probably polymers, were obtained as the major by-products in the reaction.

The structure of these photoadducts were determined by various physical methods,[2-4] including ^{13}C-NMR spectroscopy, which is vital for the determination of the reaction sites. Photoadducts I-III do not show the characteristic vibrational fine structure of conjugated polyacetylenes in the UV absorption spectra as shown in Figure 1. The absorption maxima were red shifted in I and blue shifted in II and III. IR spectra show acetylenic stretching bands, with medium intensity in I and weak in II and III. Mass spectra of all the photoadducts show M^+ peaks, indicating that the photoadduct I is formed by addition of one DMFu, while II and III are formed by addition of two DMFu molecules to one molecule of DPB. We would like to reassign the correct structure of the products as I, II, and III on the contrary to the structure reported in reference 1(a).[5]

As shown in Figure 2, the 1:1 photoadduct(I) is initially formed and extended irradiation of the solution results in decrease of I and the formation of 1:2 photoadducts(II and III) indicating that I is the primary photoadduct and II and III are the secondary photoadducts. Photolysis of pure I with DMFu in THF results in the formation of II and III strongly supporting that I is the primary and II and III are the secondary photoadducts.

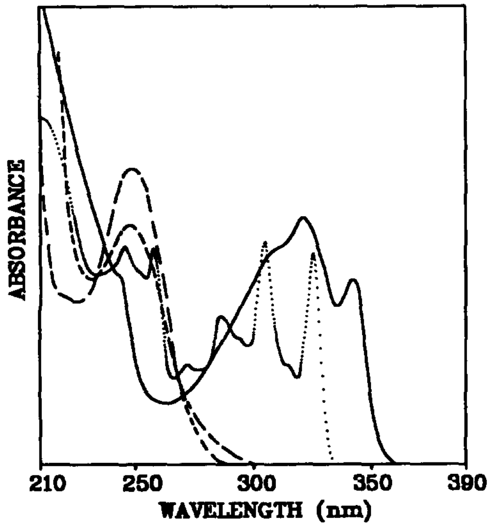


Figure 1. UV absorption spectra of DPB (. . . . .), I(———), II(- - - - -), and III (— —) in Methanol.

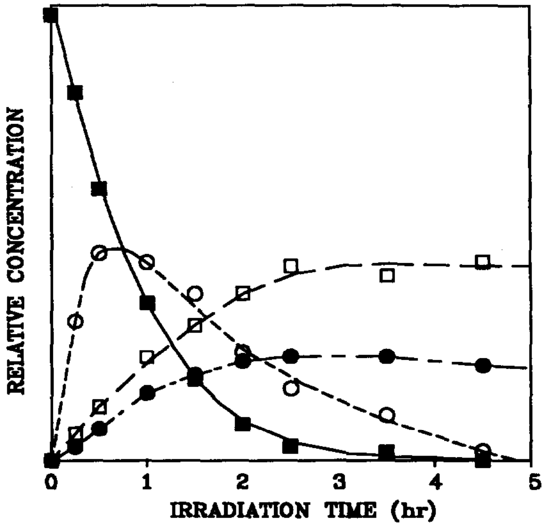


Figure 2. Reaction profile of the photoreaction against irradiation time: DPB(———), I(- - - - -), II(———), and III(— — —).

The photocycloaddition reaction of **DPB** with **DMFu** to give **I** is efficiently quenched by tetracene(E_t=29.3 kcal/mol) as the quantum yields decrease linearly with increasing tetracene concentration showing a large $k_q\tau$ of 2,400 M^{-1}(Figure 3) indicating that the reaction proceeds from the triplet excited state. When oxygen is present(aerated solution, Table 1), the photoreaction is efficiently quenched, supporting the triplet reaction mechanism.

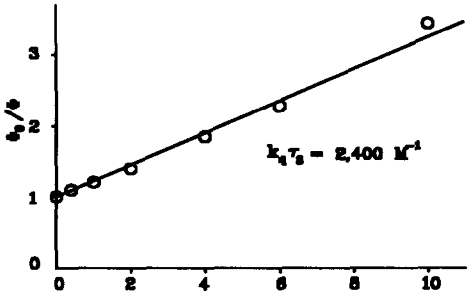


Figure 3. Triplet quenching of DPB/DMFu photoreaction with tetracene.

Table 1. Oxygen effect on the primary and secondary photoreactions at 313 nm.

CONDITION REACTION	deaerated	aerated
$\mathrm{DPB/DMFu} \xrightarrow{h\nu} \mathrm{I}$	1	*0.20
$\mathrm{I/DMFu} \xrightarrow{h\nu} \mathrm{II}$	1	0.97
$\mathrm{I/DMFu} \xrightarrow{h\nu} \mathrm{III}$	1	0.25

*Relative quantum yields with respect to deaerated solutions

The oxygen effects on the photoreaction of **I** with **DMFu** to give **II** and **III** are summarized in Table 1. No significant effect on the quantum yield of **II** was observed but that of **III** decreased to 25% in aerated solution indicating that **II** and **III** are produced *via* singlet and triplet excited state of **I**, respectively. The fluorescence of **I** is efficiently quenched by **DMFu**($k_q\tau_f$= 5 M^{-1}) (Figure 4) strongly supporting that one of the secondary product(**II**) is produced *via* the singlet excited state of **I**.

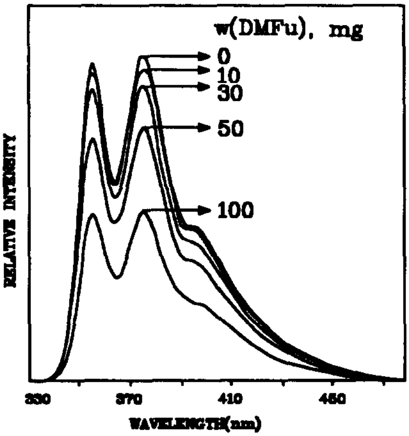
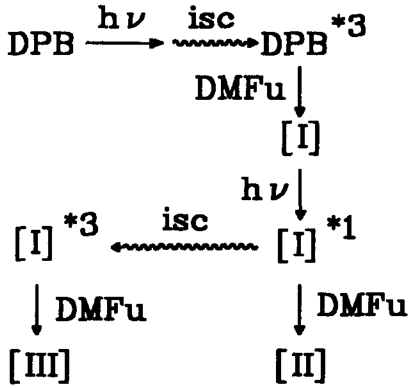


Figure 4. Fluorescence quenching of I by DMFu.



Scheme 2

From these results, we propose a plausible photoreaction mechanism as shown in Scheme 2. Triplet excited state of **DPB** reacts with **DMFu** initially to give the primary product(**I**). **I** absorbs a second photon to react with another molecule of **DMFu** to produce the novel adducts **II** (from singlet excited state) and **III** (from triplet excited state). No evidence of exciplex formation between **I** and DMFu was observed even though there seems to be some interaction between singlet excited state of **I** and carbonyl group of DMFu to give **II**.

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Notes and References

1. (a) Shim, S.C.; Kim, S.S., *Tetrahedron Lett.*, **26**(6), 765(1985). (b) Lee, T.S.; Lee, S.J.; Shim, S.C., *J. Org. Chem.*, **55**, in press(1990). (c) Shim, S.C.; Lee, T.S., *J. Org. Chem.*, **53**, 2410(1988). (d) Shim, S.C.; Lee, T.S., *Chem. Lett.*, 1075(1986). (e) Shim, S.C.; Lee, T.S., *Bull. Kor. Chem. Soc.*, 7(4), 304(1986).
2. **I**:UV(MeOH), λ_{max}=342, 321, 310(sh), 243(sh) nm; IR (NaCl), 3060-3025, 2952, 2195, 1735, 1572, 1439, 1218, 1027, 759, 691 cm^{-1}; ^{1}H-NMR(200 mHz, $CDCl_3$), δ=7.76-7.35(m, 10H), 4.17/4.03(d/d, J=2.14Hz, 1H/1H), 3.79(s, 3H), 3.74(s, 3H); ^{13}C-NMR(50 MHz, $CDCl_3$) δ=171.88, 171.35, 148.62, 133.29, 132.43, 130.04, 129.62, 129.17, 126.72, 123.18, 119.66, 98.30, 84.11, 52.96, 52.93, 48.84, 47.03 ppm; MS(70 eV), m/e=346(M$^+$, 28.9%), 331(M$^+$-CH_3, 1.6%), 314(64.6%), 299(6.8%), 286(76.3%), 271(2.4%), 226(51.5%), 215($C_{17}H_{11}$, 100%), 202(M$^+$-DMFu, 22.3%).
3. **II**:UV(MeOH), λ_{max}=248 nm; IR (NaCl), 3100-3020, 2950, 2844, 2227(w), 1735, 1439, 1289, 1001, 905, 757 cm^{-1}; ^{1}H-NMR(300 mHz, $CDCl_3$), δ=7.37-7.26(m, 10H), 6.80/6.27(d/d, J=15.6 Hz, 1H/1H), 4.28/4.19(d/d, J=9Hz, 1H/1H), 3.77(s, 3H), 3.72(s, 3H), 3.36(s, 3H), 3.26(s,3H); ^{13}C-NMR(75 MHz, $CDCl_3$) δ=170.86, 169.41, 165.79, 143.27, 136.30, 131.73, 128.56, 128.15, 127.97, 127.65, 125.97, 124.50, 122.28, 105.81, 92.16, 85.60, 82.44, 54.96, 52.04, 51.90, 51.66, 51.77, 51.27, 42.34 ppm; MS(70 eV), m/e=490(M$^+$, 1.5%), 346(M$^+$-DMFu, 3.6%), 313(85.3%), 287(28.0%),226(6.0%), 202(. M$^+$-2DMFu, 3.8%), 105(100%), 77(70%).
4. **III**:UV(MeOH), λ_{max}=250, 220(sh) nm; IR (NaCl), 3100-3015, 2954, 2849, 2226(w), 1736, 1439, 1213, 1025, 760cm^{-1}; ^{1}H-NMR(300 mHz, $CDCl_3$), δ=7.44-7.11(m, 10H), 4.03/3.97(d/d, J=9.10Hz, 1H/1H), 4.23/3.97(d/d, J=9.43 Hz, 1H/1H), 3.75(s, 3H), 3.73(s, 3H), 3.73(s, 3H), 3.67(s, 3H), 3.10(s, 3H) ; ^{13}C-NMR(75 MHz, $CDCl_3$) δ=171.66, 170.87, 170.72, 170.58, 137.90, 132.30, 132.21, 129.12, 128.93, 128.76, 128.44, 128.09, 127.43, 122.96, 91.50, 85.14, 55.64, 52.96, 52.82, 52.35, 47.78, 46.45, 46.14, 44.70, 44.25 ppm; MS(70 eV), m/e=490(M$^+$, 3.1%), 460(4.6%), 431(16.6%), 372(72.1%), 339(37.1%), 307(16.4%), 252(83.6%), 239(24.6%), 226(19.7%), 202(. M$^+$-2DMFu, 6.5%), 59(100%).
5. The bicyclobutene derivative(7 in 1(a)) must be replaced by cyclobutene derivative([I] in this paper) from various physical data(ref. 3). MS and ^{13}C-NMR were not available at our institute in 1985. UV absorption and fluorescence spectra of 7 exactly mach those of [I]. At initial stage of photolysis, this photoadduct is the only major product.

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