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PHOTOADDITION REACTIONS OF 1,4-DIPHENYLBUTADIYNE WITH OLEFINS

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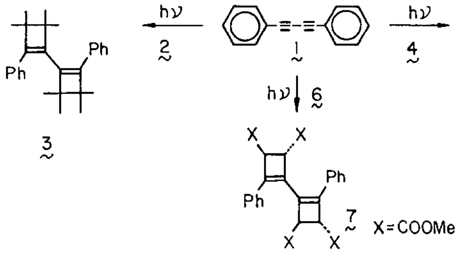
Abstract: 1,4-Diphenylbutadiyne(DPB) and several olefins such as 2,3-dimethyl-2-butene, 1,4-cyclohexadiene and dimethyl fumarate were irradiated with 300 nm UV light to obtain interesting cross-cycloaddition products.

Certain naturally occurring poly-ynes have been reported to be phototoxic to a variety of microorganisms, human skin fibroblasts, mosquito larvae and paramecium(1-5). For example, phenylheptatriyne(PHT) is phototoxic to many organisms containing membranes, including eukaryotic cells, fungi, bacteria and viruses in the presence of long wave UV(6). PHT does not induce crosslinks in calf thymus DNA in the presence of UVA in contrast to 8-methoxypsoralen phototoxicity which involves crosslinks in DNA(1,6,7). Instead, certain poly-yne such as PHT exerts its phototoxic action via the viral membrane damage and as a consequence the viral genome, DNA or RNA, is unable to replicate(8). Nothing is known about the photochemistry of poly-ynes even though it is essential to understand the molecular mechanism of phototoxicity of the compounds.

We now report for the first time the noble photoaddition reactions of DPB with some olefins such as 2,3-dimethyl-2-butene, 1,4-cyclohexadiene and dimethyl fumarate as a model photoreaction of poly-ynes with membranes of various organisms.

When a degassed n-hexane solution of DPB 1 and 2,3-dimethyl-2-butene 2, an electron rich olefin, is irradiated with 300 nm UV light, a cross-cycloaddition product 3 is obtained(9).



The first excited singlet state of acetylene is known to be a trans-vinyl biradical(10,11). Our results can be interpreted in terms of a biradical intermediate. Conjugated poly-ynes exhibit characteristic electronic absorption spectra with the most prominent feature being a very high intensity band with well-defined vibrational fine structure(12,13) but the new compound 3 does not show these typical poly-yne vibrational bands. The new absorption band observed at 345 nm is due to the conjugation of the two phenyl groups at 1,4-position and a newly produced 1,3-diene moiety(14). The [2+2] photoadduct 3 fluoresces while DPB does not.

The photoreaction of DPB 1 and 1,4-cyclohexadiene 4 with 300 nm UV light produces a very interesting compound 5(15).

Finally, the analogous photochemical reaction of DPB 1 with dimethyl fumarate 6, an electron deficient olefin, in dichloromethane solution also yields a [2+2] photocycloadduct 7(16).

The fluorescence emission bands of 1:2 photoadducts are governed by the olefins added to DPB, which shift to the shorter wavelength in the sequence: 5 > 3 > 7 (Figure 1).

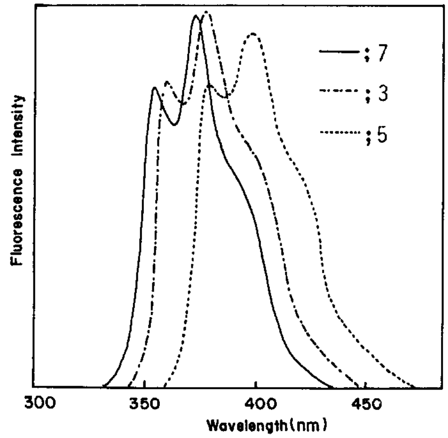


Figure 1. Change of fluorescence spectra of the photoadducts in methanol at r.t.

The emission maximum of 5 is shown at longer wavelength than that of 7 by 25 nm. The results indicate that the increasing electron-withdrawing force of the side groups on the fluorophores shifts the fluorescence emission spectra towards shorter wavelength. The photocycloaddition of DPB to various olefins suggests that phototoxic polyynes cycloadd to pyrimidine bases in RNA or DNA on irradiation with long wave UV and results in inactivation of replication activity of RNA or DNA. These studies are under progress in this laboratory.

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9. 3: UV(methanol), λ_{max} = 345, 323, 300, 282, 245, 235, 223 and 205 nm; IR(NaCl), 3020-3080 (ν_{C-H} in phenyl ring), 2860-2980(ν_{C-H} of C-CH_3), 1360-1400(δ_{C-H} of C-CH_3) and 1573 cm^{-1} ($\nu_{C=C}$ of cyclobutene ring); ^{1}HNMR(80 MHz, $CDCl_3$), δ = 7.33-8.27(m, $2C_6H_5$), 1.73(s, $4CH_3$) and 1.60 ppm(s, $4CH_3$); MS(70 eV), m/e=286($C_{22}H_{22}^+$, $M^+-C_6H_{12}$), 271($C_{21}H_{19}^+$, $M^+-C_6H_{12}-CH_3$, 100 %) and 202($M^+-2C_6H_{12}$); Elemental Analysis, C/H=90.73/8.94(Calculated, 90.81/9.19).
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14. UV spectrum of the compound 3 was compared with that of 1,4-diphenylbutadiene from Sadtler, (1088 UV).
15. 5: UV(methanol), λ_{max}=333, 313 and 222 nm; IR, 3030-3090(ν_{C-H} of phenyl ring), 2860-2965 (ν_{C-H} of aliphatic moiety), 1030(deformation mode of the cyclopropane ring) and 840 cm^{-1} (δ_{C-H} of the cyclopropane ring); ^{1}HNMR(80 MHz, $CDCl_3$), δ=7.22-7.95(m, $2C_6H_5$), 7.03(d, 2x 1H, J=16 Hz), 6.35(d, 2X 1H, J=16 Hz), 6.68(d, 2x 1H, J=12 Hz), 5.90(d, 2x 1H, J=12 Hz), 1.53(s, broad, 2x 2H) and 1.26 ppm(s, broad, 2x 2H); MS(70 eV), m/e=362(M^+), 202($C_{16}H_{10}^+$, $M^+-2C_6H_8$) and 204($C_{16}H_{12}^+$, 100 %).
16. 7: UV(methanol), λ_{max} = 341, 321 and 232 nm; IR, 1730, 1735 cm^{-1} ($\nu_{C=O}$); ^{1}HNMR(80 MHz, $CDCl_3$), δ=7.25-7.80(m, $2C_6H_5$), 4.17(d, 2x 1H, J=3 Hz), 4.03(d, 2x 1H, J=3 Hz), 3.81(s, $2CH_3$) and 3.76 ppm(s, $2CH_3$).

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