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Photocycloaddition Reaction of 5(E)-Styryl-1,3-dimethyluracil with Some Olefins#

Sang Chul SHIM* and Eun Ju SHIN
Department of Chemistry, Korea Advanced Institute of Science and Technology,
P.O. Box 150, Chongryangni, Seoul 131, Korea

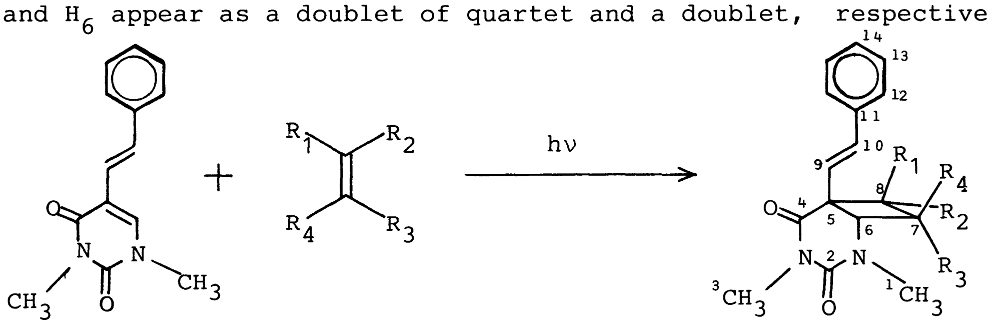
Photolysis of 5(E)-styryl-1,3-dimethyluracil(5(E)-SDU) with some olefins, such as tetramethylethylene, methyl crotonate, dimethyl ethylidenemalonate, and dimethyl maleate in dichloromethane yields [2+2] cycloadducts along with E⇄Z photoisomerization and photocyclization products of 5-SDU. The [2+2] cycloaddition reaction with olefins occurs on the 5,6-double bond of uracil ring rather than the expected central double bond.

Extensive research on the photochemical [2+2] cycloaddition has been accomplished and the intermediacy of exciplexes is firmly established.[1,2] Photocycloaddition of stilbene to numerous olefins which are different in electron affinity has been well studied and are known to occur via singlet exciplex intermediates formed between electronically excited stilbene and ground state olefins.[3-5] However, the photocycloaddition reaction of the stilbene derivatives which contain hetero-atoms or are unsymmetrically substituted has been paid little attention. 5(E)-Styryl-1,3-dimethyluracil(5(E)-SDU), in which one phenyl ring in stilbene is replaced with a pyrimidine base, has both (n,π^*) and (π,π^*) excited states resulting in the different photochemical and photophysical properties from stilbene. It was previously studied that E⇄Z photoisomerization[6)] and photocyclization[7)] of 5(E)-SDU occur via the excited singlet state as those of stilbene. The photocycloaddition reaction of 5(E)-SDU, which has two reaction sites of the 5,6-double bond of uracil ring and the central C=C double bond, with some olefins with various electron affinities is investigated.

A dichloromethane solution of 5(E)-SDU and tetramethylethylene(TME, <u>1</u>) is irradiated with 350 nm light. The major product from the photoreaction mixture including E⇄Z photoisomerization and photocyclization products is isolated in 14.6 % yield by preparative TLC or silica gel column chromatography and characterized by the various spectroscopic methods. Mass spectrum shows molecular ion peak at m/e 326 which is the sum of the molecular weight of 5(E)-SDU and that of TME. The base peak appears at m/e 242 which is the molecular weight of 5(E)-SDU and the peak at m/e 84 which is the molecular weight of TME indicating the photoproduct (<u>1a</u>) to be a 1:1 adduct of 5(E)-SDU and TME. The aliphatic C-H stretching band at 2900 cm^{-1} is more intense and one of the carbonyl stretching bands($\nu_{C=O}$ 1680 and 1710 cm^{-1}) is red-shifted compared to those in 5(E)-SDU($\nu_{C=O}$ 1650 and 1710 cm^{-1}), probably due to the saturation of C=C double bond adjacent to the carbonyl group.

#Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

The results suggest that the photoproduct is a [2+2] cycloaddition product between the 5,6-double bond of uracil moiety in 5(E)-SDU and TME. UV spectrum in methanol shows two bands at 227 nm(ε 8170) and 310 nm(ε 30) with disappearance of 318 nm band of 5(E)-SDU. ^{1}H NMR spectrum in $CDCl_3$shows four singlets of methyl protons at 1.07(s,3H), 1.19(s,3H), 1.32(s,3H),and 1.41(s,3H), a singlet of 1-N-methyl protons at 2.48(s,3H),a singlet of cyclobutane ring proton at 3.37(s,1H), a singlet of 3-N-methyl protons at 3.52(s,3H), two doublet of olefinic protons at 6.12(d,1H,11.9 Hz) and 7.01(d,1H,11.9 Hz), and multiplet of benzene ring protons at 7.29 ~ 7.6 ppm(m,5H). The data further supports the formation of a [2+2] cycloadduct between uracil moiety and TME, especially from the large shift of 1-N-methyl protons relative to those of 5(E)-SDU and remainder of olefinic protons in styrene moiety. ^{13}C NMR spectrum of 1a in $CDCl_3$ shows 18 peaks in agreement with the cycloadduct.$^{8)}$ Irradiation of a dichloromethane solution of 5(E)-SDU in the presence of excess methyl crotonate(2) with 350 nm light affords three isomeric cycloadducts 2a, 2b, and 2c in a ratio of 64:8:1 in total yield of 23.5 %.$^{9)}$ IR spectra show carbonyl stretching bands of ester group in 2 and amide groups in 5(E)-SDU and in UV spectra absorption band around 225-230 nm is observed as in the photocycloadduct with TME. NMR spectra indicate these materials to be cycloadducts of 5(E)-SDU with 2, although the orientation of the compounds are not definitely assigned. For the major cycloadduct 2a, H_8 appears as a multiplet, H_6 as a doublet(J=9 Hz) and is cis to H_7, and H_7 as a doublet of doublet and is cis to H_6 and trans to H_8. H_6 and H_8 lie apart from the shielding region of the double bond of styrene and thus shift downfield compared with those in 2c. H_7 in 2a has lower chemical shift than that in 2c because of shielding by the double bond of styrene under compulsion of the puckered cyclobutane ring. In 2b, H_8 and H_7 appear as multiplet with similar chemical shifts and H_6 as a doublet(J=8 Hz) and has cis stereochemistry to H_7, and in ^{13}C-NMR ester carbonyl carbon, C_7, C_8, C_{10}, and C_{11} of 2b are greatly shifted relative to those of 2a and 2c in agreement with the structural difference from 2a and 2c, while in the more congested adduct 2c which is obtained in trace amounts, H_8 and H_6 appear as a doublet of quartet and a doublet, respectively, and H_7 with



5(E)-SDU

1:R_1,R_2,R_3,R_4=CH_3
2:R_1=CH_3,R_2,R_4=H,R_3=CO_2CH_3
3:R_1=CH_3,R_2=H,R_3,R_4=CO_2CH_3
4:R_1,R_4=H,R_2,R_3=CO_2CH_3

1a:R_1,R_2,R_3,R_4=CH_3
2a:R_1=CH_3,R_2,R_4=H,R_3=CO_2CH_3
2b:R_1=CO_2CH_3,R_2,R_4=H,R_3=CH_3
2c:R_1,R_3=H,R_2=CH_3,R_4=CO_2CH_3
3a:R_1=CH_3,R_2=H,R_3,R_4=CO_2CH_3
3b:R_1=H,R_2=CH_3,R_3,R_4=CO_2CH_3
4a:R_1,R_4=H,R_2,R_3=CO_2CH_3

trans stereochemistry to H_6 and H_8 appears as a triplet. Photocycloaddition reaction of 5(E)-SDU with dimethyl ethylidenemalonate in dichloromethane yields two isomeric cycloadducts 3a, 3b in 3:2 ratio.[10] In the less congested major adduct 3a, the chemical shifts of H_8 as a quartet and H_6 as a singlet are shifted downfield compared with those in 3b due to being apart from the shielding region of the double bond of styrene. A cycloadduct 4a[11] is obtained in the photoreaction with dimethyl maleate. Each of H_6 and H_8 appears as a doublet and H_7 as a triplet. All cis stereochemistry for H_6, H_7, and H_8 may be deduced from the relatively large coupling constant and is favorable due to the overlap between C_4=O group of uracil ring and C=O group of R_2. As H_7 of 4a containing two ester groups is predicted to have higher chemical shift than that of 2a or 2c containing one methyl and one ester group and has similar chemical shift to that in 2a rather than 2c, it is inferred that H_7 of 4a lies in the shielding region by the double bond of styrene as that of 2a. H_6 and H_8 of 4a lying in the shielding region of the double bond of styrene have relatively high chemical shift because the puckered cyclobutane ring forces H_7 to lie inward but H_6 and H_8 to lie outward from cyclobutane ring. Above results indicate that 5(E)-SDU undergoes [2+2] photocycloaddition reaction to several electron-rich and electron-poor olefins similar to stilbene.

As shown in Table 1, the fluorescence quenching of 5(E)-SDU by olefins is not efficient in contrast to stilbene. Especially, as methyl crotonate and dimethylethylidene malonate are used as quencher olefins in dichloromethane, no quenching of fluorescence of 5(E)-SDU is observed up to olefin concentration of 2 M. Therefore, it is inferred that [2+2] photocycloaddition reaction of 5(E)-SDU with olefins may proceed via the excited triplet state rather than excited singlet state.

Table 1. Fluorescence quenching of 5(E)-SDU with some olefins in dichloromethane at room temperature [a)]

Olefin	$k_q\tau$/ M^{-1}
TME[b)]	0.045
Methyl crotonate	no quenching
Dimethyl ethylidenemalonate	no quenching
Dimethyl maleate	0.282

a)Concentration of 5(E)-SDU is 2.5×10^{-4} M. Excitation wavelength is 370 nm. Olefin concentration is used up to 2 M if not noted otherwise. b)Tetramethylethylene(TME) is used up to 4 M.

While cyclobutane ring is formed on the central C=C double bond in stilbene, photocycloaddition of 5(E)-SDU occurs on the 5,6-double bond of uracil ring. Short irradiation of a dichloromethane solution of 5(E)-SDU and TME produces an unidentified material which has λ_{max} of 270 nm in UV spectrum and the prolonged irradiation till the reactant is completely exhausted results in the formation of adduct 1a with the remarkable decrease of this material. Cycloadduct is not formed if the irradiation time is short or the monochromatic light of 366 nm is used. It is very likely that the photocycloaddition reaction of 5(E)-SDU with olefin proceeds indirectly via an intermediate.

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8) 1a: Pale yellow oil; ^{13}C NMR δ 19.3, 21.1, 23.4, 24.4, 27.7, 35.0, 43.7, 45.6, 52.3, 61.7, 127.2, 128.0, 128.3, 131.0, 131.4, 137.1, 152.2, 171.1 ppm; ^{1}H NMR δ 1.07, 1.19, 1.32, 1.41(R_1-R_4), 2.48(s,3H,N_1-CH_3), 3.37(s,1H,H_6), 3.52(s,3H, N_3-CH_3), 6.12(d,11.9 Hz,1H,H_9), 7.01(d,11.9 Hz,1H,H_{10}), 7.29-7.6(m,5H,phenyl) ppm.

9) 2a: White solid; UV(methanol) λ_{max} 300(very weak and broad) and 225 nm; IR(NaCl) 3040, 2980, 1745, 1720, 1680, 1380, 1295 cm^{-1}; ^{13}C NMR δ 17.2, 28.7, 34.5, 38.6, 49.4, 50.1, 52.7, 55.3, 128.2, 128.6, 129.0, 129.8, 133.5, 137.2, 152.7, 172.2, 172.9 ppm; ^{1}H NMR δ 1.42(d,7.4 Hz,R_1), 2.43(s,N_1-CH_3), 2.93(dd,4.4 Hz,9.0 Hz, H_7), 3.38(dq,4.4 Hz,7.4 Hz,H_8), 3.42(s,N_3-CH_3), 3.78(s,R_3), 3.87(d,9 Hz,H_6), 6.03(d,12 Hz,H_9), 7.03(d,12 Hz,H_{10}), 7.23-7.51(m,phenyl) ppm. 2b: oil; ^{13}C NMR δ 17.1, 28.8, 35.2, 42.0, 50.7, 51.2, 52.9, 57.3, 128.2, 128.6, 129.0, 132.1, 133.4, 152.5, 170.1, 173.0 ppm; ^{1}H NMR δ 1.35(d,6.2 Hz,R_3), 2.62(s,N_1-CH_3), 2.66-2.69(m,H_7 and H_8), 3.34(s,N_3-CH_3), 3.67(s,R_1), 3.70(d,8 Hz,H_6), 6.05(d, 11.6 Hz,H_9), 6.88(d,11.6 Hz,H_{10}), 7.21-7.49(m,phenyl) ppm. 2c: oil; ^{13}C NMR δ 14.5, 28.9, 34.4, 34.7, 50.3, 52.7, 52.9, 56.1, 128.2, 128.7, 129.0, 129.2, 133.6, 136.9, 152.7, 172.2, 172.9 ppm; ^{1}H NMR δ 1.11(d,7.6 Hz,R_2), 2.48(s, N_1-CH_3), 2.91(dq,3.5 Hz,7.6 Hz,H_8), 3.33(d,3.4 Hz,H_6), 3.45(s,N_3-CH_3), 3.94(t, 3.5 Hz,H_7), 3.94(s,R_4), 5.88(d,11.6 Hz,H_9), 6.95(d,11.6 Hz,H_{10}), 7.26-7.56(m, phenyl) ppm.

10) 3a: oil; UV(methanol) λ_{max} 310 and 227 nm; IR(NaCl) 3040, 2970, 1745, 1720, 1680, 1390, 1280 cm^{-1};^{13}C NMR δ 13.0, 28.6, 34.7, 41.2, 48.7, 53.2, 53.7, 57.7, 61.7, 128.2, 128.6, 129.0, 129.1, 134.2, 137.0, 152.4, 169.0, 169.1, 172.4 ppm; ^{1}H NMR δ 1.29(d,7.6 Hz,R_1), 2.41(s,N_1-CH_3), 3.34(s,N_3-CH_3), 3.61(s,R_4), 3.79(q, 7.6 Hz,H_8), 3.89(s,R_3), 4.39(s,H_6), 5.96(d,12.0 Hz,H_9), 7.04(d,12.0 Hz,H_{10}), 7.25-7.54(m,phenyl) ppm. 3b: oil; ^{13}C NMR δ 12.1, 28.3, 34.5, 45.3, 48.8, 53.2, 59.8, 61.0, 128.3, 128.7, 129.0, 131.6, 133.9, 136.7, 152.9, 167.9, 169.3, 171.3 ppm; ^{1}H NMR δ 1.50(d,7.3 Hz,R_2), 2.54(s,N_1-CH_3), 2.94(q,7.3 Hz,H_8), 3.39 (s,N_3-CH_3), 3.60(s,R_4), 3.93(s,R_3), 4.03(s,H_6), 6.05(d,11.6 Hz,H_9), 6.67(d, 11.6 Hz,H_{10}), 7.23-7.56(m,phenyl) ppm.

11) 4a: UV(methanol) λ_{max} 300 and 237 nm; IR(NaCl) 3020, 2970, 1750, 1720, 1680, 1390, 1360, 1290 cm^{-1}; ^{13}C NMR δ 29.2, 35.0, 46.0, 49.1, 50.4, 52.7, 52.9, 57.4, 127.4, 128.3, 128.7, 129.1, 134.7, 136.7, 151.8, 170.7, 171.1 ppm;^{1}H NMR δ 2.65(s,N_1-CH_3), 3.30(t,9.1 Hz,H_7), 3.40(s,N_3-CH_3), 3.82(s,R_2), 3.90(s,R_3), 3.98(d,9.6 Hz,H_8), 4.33(d,9.1 Hz,H_6), 5.84(d,12.0 Hz,H_9), 6.96(d,12.0 Hz,H_{10}), 7.29-7.54(m,phenyl) ppm.

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