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PHOTOCHEMICAL REACTION OF NAPHTHALENE WITH CIS- AND TRANS-CYCLOOCTENE[1)]

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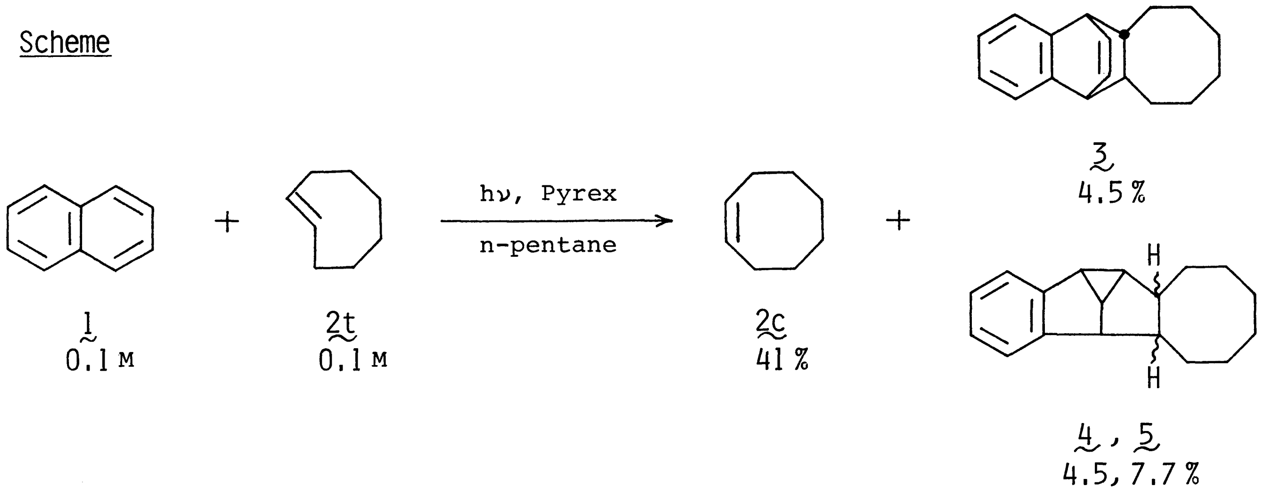
Irradiation(>300 nm) of naphthalene(**1**, 0.1 M) and _trans_-cyclooctene(**2t**, 0.1 M) yielded the _cis_-isomer(**2c**) and three 1:1 adducts **3**-**5**, whereas **2c**(0.1 M) did not give any products under the same conditions. A singlet mechanism is proposed on the basis of Stern-Volmer studies on fluorescence, singlet lifetime, and the adduct formation.

Recently, non-vertical singlet photosensitization of simple alkenes by aromatic esters has been reported from these laboratories.[3)] The mechanism involves the formation of a singlet exciplex of an alkene with an excited aromatic ester and the subsequent rotation about the C=C double bond of the alkene moiety in the exciplex, giving rise to a twisted singlet of the alkene. However, since most aromatic esters are non-emissive, we could not obtain definitive spectroscopic evidence for the involvement of sensitizer singlet.

Naphthalene has a long singlet lifetime(~100 ns) and a fairly high singlet energy (92 kcal/mol) but possesses a low triplet one (61 kcal/mol),[4)] and is therefore a potential singlet sensitizer for simple alkenes. Mechanism of fluorescence quenching of naphthalenes by conjugated dienes[5,6)] and quadricyclene[7)] has been well established. The chemical consequence of the quenching, usually adduct formation and/or photosensitization, is also well known.[5-8)] On the other hand, similar fluorescence quenching by simple alkenes is believed to be much less effective, and the resultant chemistry as a consequence of the quenching, if any, is relatively unexplored. We wish now to report our results on the effective quenching of naphthalene fluorescence by _trans_-cyclooctene and the chemical consequence of the singlet quenching.[9)]

Photochemical Reactions. Irradiation at >300 nm of a pentane solution of naphthalene(**1**, 0.1 M) containing _trans_-cyclooctene(**2t**, 0.1 M) under a nitrogen atmosphere gave _cis_-cyclooctene(**2c**) and three 1:1 adducts **3**-**5**.[10)] The product yields and the substrate recoveries reached stationary state in spite of the presence of remaining **1** and produced **2c**, when most **2t** was consumed after 8 h irradiation. This result is consistent with the observation that irradiation of **1**(0.1 M) with **2c**(0.1 M) under the same conditions did not produce detectable yields of any product. However, **2c**(7.7 M) did form 1:1 adducts[9)] with **1** in good yield (>40 %) after irradiation up to 32 h, although no **2t** was detected on vpc.

Scheme



These observations demonstrate that the trans→cis photoisomerization of cyclooctene is irreversible and the excited naphthalene reacts with 2c only at much higher concentrations.

The adducts[11)] from the reaction of 1 with 2t were isolated by column chromatography over silica gel and the subsequent preparative vpc, and were subjected to the spectral analyses. The structures of the adducts 3-5 rest on the following spectral and chemical evidence. Adduct 3: CI-MS(methane), m/z(relative intensity) 239(54), 129(100); EI-MS(70 ev), m/z 238(3), 128(100); IR(neat), 3040, 3000, 2900, 1630(C=C), 1600(Ph), 1460, 700($^{H}\diagdown C{=}C\diagup^{H}$)cm^{-1}; ^{1}H NMR(100 MHz, $CDCl_3$, TMS), δ 7.10(4H, m), 6.60(1H, ddd, J=8,5,1.5Hz), 6.35(1H, ddd, J=8,5,1.5Hz), 3.60(1H, ddd, J=5,1.5, 1Hz), 3.50(1H, ddd, J=5,1.5,1Hz), 1.47(14H, br.); ^{13}C NMR(15 MHz, $CDCl_3$, TMS), δ 146.3(s), 142.4(s), 137.6(d), 133.3(d), 126.0(d, double intensity), 125.5(d), 123.1 (d), 49.5(d), 49.3(d), 45.5(d), 43.9(d), 38.1(t), 37.3(t), 28.3(t, double int.), 25.1(t, double int.). The adduct 3 was hydrogenated over 5% Pd/C in cyclohexane for 4 hr to give a hydrogenated compound(m/z 240), and photodecomposed to naphthalene and cyclooctene in good yields after 30 min irradiation in a quartz tube, although no change was observed under irradiation in a Pyrex tube.[11)] The presence of an olefinic double bond is clearly indicated and therefore the adduct 3 is infered to be a 1,2- or 1,4-adduct. ^{1}H NMR pattern of the olefinic protons excludes the possibility of the 1,2-adduct structure for 3.[12)] The trans-configuration of the cyclooctene moiety is deduced from the non-equivalent olefinic and allylic protons/carbons on ^{1}H and ^{13}C NMR spectra. Adduct 4: CI-MS, m/z 239(100), 129(45); EI-MS, m/z 238(28), 128(100); IR(neat), 3050, 3030, 3000, 2920, 2845, 1600(Ph), 1460, 1009(△), 985 cm^{-1}; ^{1}H NMR, δ 6.96(4H, m), 3.15(1H, d, J=6 Hz), 2.85(1H, q, J=6 Hz), 2.5(1H, br. m), 2.14(1H, q, J=6 Hz), 1.90(1H, t, J=6 Hz), 0.7-1.7(13H, br.). Adduct 5: CI-MS, m/z 239(100), 129(90); IR(neat), 3040, 3000, 2900, 2840, 1600(Ph), 1445, 1005(△), 907 cm^{-1}; ^{1}H NMR, δ 6.99(4H, m), 3.30(1H, t, J= 5 Hz), 2.78(1H, tdd, J=7, 5,5Hz), 2.25(2H, m), 1.40(14H, br.). The adducts 4 and 5 were not hydrogenated under the same conditions mentioned above, and photodecomposed to miscellaneous products including a trace amount of naphthalene. Although it is evident from the above data that 4 and 5 are 1,3-addition products[13)] shown in Scheme, their stereochemistries are not established at present.

Table Quenching Rate Constants (k_q) in Pentane at Room Temperature

Compd	Fluorescence quenching$^{a)}$		Lifetime measurement$^{b)}$		Adduct formation$^{c)}$
	Degassed$^{d,e)}$	Aerated$^{f)}$	Degassed$^{d,e)}$	Degassed$^{d,g)}$	Degassed$^{d,g)}$
2c	0.083×10^{-7}	-	0.125×10^{-7}	-	0.10×10^{-7}
2t	2.48×10^{-7}	2.56×10^{-7}	2.59×10^{-7}	2.61×10^{-7}	3.8×10^{-7}

a) Excitation: 305 nm; observation: 336 nm. b) Excitation: 311 nm; observation: 336 nm. c) Irradiation with a 450 W Hanovia medium pressure Hg lamp was performed in a merry-go-round apparatus at 313 nm through a K_2CrO_4 solution filter; conversion<5 %. d) Degassed up to 1×10^{-5} Torr through five freeze-pump-thaw cycles. e) [**1**] = 9.1×10^{-5} M; τ = 117 ns. f) [**1**] = 7.2×10^{-4} M; τ' = 16.4 ns. g) [**1**] = 0.1 M; τ'' = 109 ns.

Quenching Studies. Fluorescence quenching$^{14)}$ of naphthalene by cis- and trans-cyclooctenes was conducted in a degassed and/or an aerated pentane solution to determine the quenching rate constant (k_q), using a Hitachi MPF-2A spectrofluorimeter. The $k_q\tau$ values are obtained from the slopes of the Stern-Volmer plots, and the k_q values are calculated by using the lifetime(τ) of naphthalene singlet in the absence of the quencher. Although the results shown in Table are somewhat different from those reported by Murov et al.,$^{6)}$ the trans quenches naphthalene singlet about 30 times faster than the cis does. The lower oxidation potential$^{3)}$ and/or V←N excitation energy$^{15)}$ of the trans may be responsible for the faster quenching by **2t**. The lifetime of naphthalene singlet was measured in the presence of the quencher **2c** or **2t** by means of a single photon counting method. Plots of τ_0/τ against quencher concentration gave good straight lines for **2c** and **2t**; similar calculations give the quenching rate constants(Table). The results are consistent with those from the fluorescence quenching. In order to obtain an evidence for the involvement of naphthalene singlet in the adduct formation, Stern-Volmer study was repeated for the adduct formation. Reciprocal of combined yield of the adducts was plotted as a function of inverse concentration of the quencher to give linear relationship.$^{16)}$ Intercept/slope gives the $k_q\tau$ value, which is in turn divided by the actual lifetime (109 ns) of naphthalene singlet under the reaction conditions to give the k_q value shown in Table. Based on the consistency of the quenching rate constant obtained in the Stern-Volmer studies of the fluorescence quenching, the lifetime measurement, and the adduct formation, it is concluded that the adduct formation proceeds via the reaction of singlet naphthalene and cyclooctene.

References

1) Singlet photosensitization of simple alkenes. part 3; see ref. 3 for parts 1 and 2.

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9) Naphthalene was reported to form two 1:1 adducts with **2c** upon irradiation: D. Brice-Smith, A. Gilvert, and B.H. Orger, Chem. Comm., 512(1966). However, the spectroscopic evidence and the detailed reaction mechanism have not been presented.

10) An additional 1:1 adduct was also obtained in 1.1 % yield, but it was not isolated due to the low yield.

11) The adduct distribution showed little change throughout the irradiation period. The isolated adducts **3**-**5** did not interconvert each other under the irradiation conditions.

12) A comparison of the ^{1}H NMR spectrum with those of compounds carrying a similar 1,2- or 1,4-adduct skeleton confirms the assignment: ref. 8; K.E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 93, 2073(1971); K. Mizuno, C. Pac, and H. Sakurai, J. Chem. Soc. Chem. Comm., 648(1974); J. Chem. Soc. Perkin Trans. 1, 2221(1975).

13) A further support for the assignment comes from the ^{1}H NMR spectra of compounds having a similar 1,3-adduct skeleton: O.L. Chapman, G.W. Borden, R.W. King, and B. Winkler, J. Am. Chem. Soc., 86, 2660(1964); K.E. Wilzwach and L. Kaplan, ibid, 88, 2066(1966).

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16) A similar treatment of the *trans*→*cis* isomerization did not fit a linear relationship, probably due to the involvement of naphthalene triplet. Participation of the triplet was supported by the finding that, in a preliminary experiment, most (70-80 %) of the *trans*→*cis* isomerization was quenched by addition of 0.001-0.1 M isoprene while the adduct yields stayed constant.

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