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PHOTOCYCLOADDITION BETWEEN INDENE AND ELECTRON-RICH OLEFINS THROUGH INDENE CATION RADICAL

Kazuhiko MIZUNO, Ryoji KAJI, and Yoshio OTSUJI
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai City, Osaka 591

Irradiation of a solution of indene and alkyl vinyl ethers in acetonitrile in the presence of 1-naphthonitrile efficiently gave two stereo-isomeric (2+2)cycloadducts; endo-2-alkoxy-2a,7a-dihydro-7H-cyclobut[a]indene and the corresponding exo-isomer. The quenching and sensitizing experiments suggested that the above cycloadducts were formed via indene cation radical.

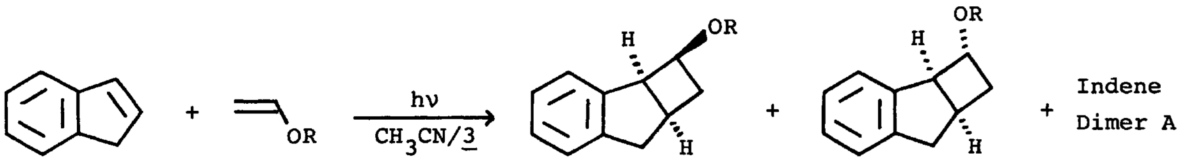
The photocyclodimerization of electron-rich olefins in the presence of an electron-accepting molecule has widely investigated from the mechanistic and synthetic view-points.1,2) In this reaction, the cation radical($D^{+\cdot}$) is first produced by the one-electron transfer from an electron-rich olefin(D) to an electron-acceptor(A), followed by the attack of D to $D^{+\cdot}$.

$$\begin{tikzcd}
 & & (D_2)^{+\cdot} \arrow[r, "A^{-\cdot}"] & D_2 \\
D + A^{*} \arrow[r] & D^{+\cdot} + A^{-\cdot} \arrow[ur, "D"] \arrow[dr, "D'"'] & & \\
(\text{or } D^{*} + A) & & (DD')^{+\cdot} \arrow[r, "A^{-\cdot}"] & DD'
\end{tikzcd}$$

D; Electron-donating olefin
A; Electron acceptor

However, the photocycloaddition between two different olefins having different electron-donating capabilities is little known.3) If an olefin(D'), whose nucleophilicity is higher than that of D, is present with D in the reaction system, then it is possible to form a hetero-cyclodimer(DD') via a hetero-dimer cation radical$(DD')^{+\cdot}$. In this communication, we report the photocycloaddition of indene(1) with alkyl vinyl ethers using 1-naphthonitrile(3) as an electron acceptor.

Irradiation of a solution4) of 1(10 mmol), ethyl vinyl ether(2b)(100 mmol), and 3 (1 mmol) in acetonitrile(50 ml) through Pyrex with a 300 W high-pressure mercury arc for 30 h gave a mixture of endo-(2+2)cycloadduct(4b) and its exo-isomer(5b) in 80 % yield along with a small amount of indene dimer A which mainly consisted of the anti-head-to-head indene dimer.2) These products were isolated by column chromatography on silica gel. Similarly, irradiation of a solution of 1 and methyl vinyl ether(2a) or trimethylsilyl vinyl ether(2c) in the presence of 3 mainly afforded the corresponding pair of the cross-cycloadducts, 4a and 5a, 4c and 5c, respectively. In the case of vinyl acetate(2d), the formation of 4d and 5d was depressed and indene dimer A was



1 2a-d 4a-d 5a-d

a; R=Me, b; R=Et, c; $R=SiMe_3$, d; R=Ac

Scheme 1

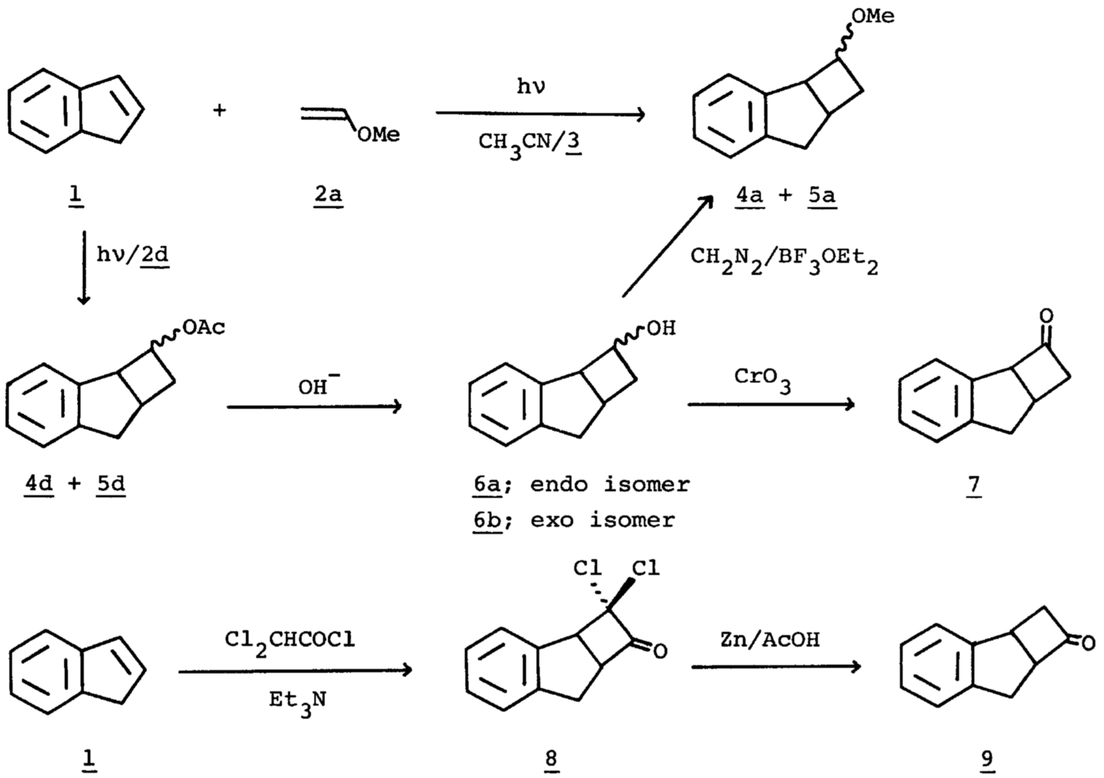
isolated as a major product.[5)] The isolated yields of the products and the exo/endo ratios in the cross-cycloadducts are shown in Table 1.

The structures of the cross-cycloadducts 4 and 5 were deduced from their analytical data and spectral properties. The positions of the methoxy and acetoxy groups in 4a, 5a, 4d, and 5d were determined by the chemical transformations shown in Scheme 2. 4a: MS(80 eV), m/e, 174(very weak), 116, 115, and 58; IR(neat) 1110 and 1130 cm^{-1}(C-O-C); NMR(CCl_4) δ=3.15(3H, s, OMe). 5a: NMR(CCl_4) δ=3.24(3H, s, OMe). 4d: MS(80 eV), m/e, 202(very weak), 116, 115, and 86; IR(neat) 1740(ester C=O), 1240, and 1045 cm^{-1}(ester); NMR(CCl_4) δ=1.82(3H, s, OAc). 5d: NMR(CCl_4) δ=2.00(3H, s, OAc). The NMR spectrum of the ketone(7) which was prepared by Jones' oxidation of the alcohol(6) obtained from the hydrolysis of 4d and 5d was different from that of the ketone(9) which was prepared by the Zn/AcOH reduction of the cycloadduct(8) obtained from 1 and dichloroketene.[6)] Moreover, the NMR spectra and the glc characteristics of the methyl ethers[7)] derived from 6a and 6b were completely agreed with those of 4a and 5a, respectively. Thus, the structures of 4a-d and 5a-d were assigned to be the endo- and exo-(2+2)cycloadducts as represented in Scheme 1.

Table 1. Isolated yields of products[a)]

Olefin	Sensitizer	Product Cross-cycloadduct (4 + 5)(%)	Ratio of exo/endo[b)] (5/4)	Indene dimer (A or B)(%)
2a(R=Me)	3	70	1.0	< 3 (A)
2a	MK[c)]	16	2.0	62 (B)
2b(R=Et)	3	80	1.4	5 (A)
2b	MK[c)]	23	2.4	70 (B)
2c($R=SiMe_3$)	3	< 30	1.0	< 5 (A)
2d(R=Ac)	3	5	2.4	20 (A)
2d	MK[c)]	34	3.8	64 (B)

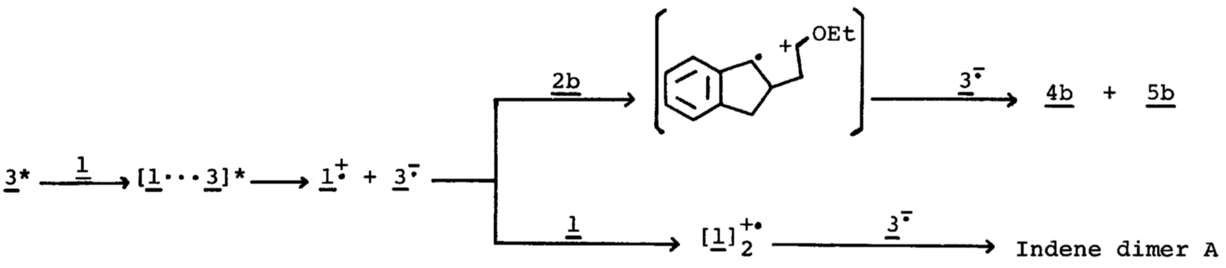
a) Yields are based on consumed indene(1). b) The exo/endo ratios were determined by the NMR or glc analyses of the reaction mixture. c) A mixture of an olefin(100 mmol), 1 (10 mmol), and Michler's ketone(MK, 1 mmol) in benzene(50 ml) was irradiated for 20 h.



Scheme 2

Some mechanistic studies were undertaken. Firstly, irradiation of an acetonitrile solution of 1, 2b, and 3 in the presence of triplet quenchers such as 1,3-pentadiene and 2-methyl-1,3-butadiene(isoprene) gave 4b and 5b as main products along with a trace amount of indene dimer A; no quenching for the formation of 4b and 5b was observed in the presence of the triplet quenchers. Secondly, irradiation of a benzene solution of 1 and 2b in the presence of Michler's ketone(a typical triplet sensitizer) without 3 preferentially gave indene dimer B which mainly consisted of the anti-head-to-head indene dimer8) and which was different from indene dimer A, although 4b and 5b were obtained as minor products(Table 1). Finally, irradiation of an acetonitrile solution of 1, 2b, and 3 containing methanol or water gave 2-methoxy- or 2-hydroxy-indane,9) and the formation of 4b and 5b was quenched under these conditions.

These results can be reasonably explained in terms of the pathways represented in Scheme 3. The interaction between the singlet excited state of 3 (3*) and the ground



Scheme 3

state of 1 produces a pair of the cation radical($1^{+\cdot}$) and the anion radical($3^{-\cdot}$) probably via an exciplex[$1\cdots3$]*.[9] The addition of the nucleophilic olefin(2b) to $1^{+\cdot}$ gives 4b and 5b. On the other hand, the reaction of $1^{+\cdot}$ with 1 whose nucleophilicity is lower than 2b gives indene dimer A which is a minor extent. However, in the Michler's ketone sensitized reaction, the triplet indene is probably produced in a primary step, and the dimerization between this excited molecule and 1 in the ground state yields indene dimer B.[8]

The proposal that 4b, 5b, and indene dimer A are produced through $1^{+\cdot}$ is supposed by the following observations: (1) The efficiency of the formation of 4b and 5b from 1 and 2b is remarkably depressed in the absence of 3 or in a non-polar solvent such as benzene.[10] (2) The addition of triethylamine, which has a lower ionization potential than 1, to the reaction system efficiently quenches the formation of 4b and 5b. The cross-cycloadduct pairs, 4a and 5a, 4c and 5c, are also produced by the reaction of $1^{+\cdot}$ with 2a and 2c, respectively, through the pathway similar to that shown in Scheme 3. However, 4d and 5d, which are obtained by the photoreaction of 1 with vinyl ester(2d) in the presence of 3, are supposed to be formed via the triplet indene since the formation of 4d and 5d was remarkably depressed by the addition of isoprene.

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