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ALLENYL(VINYL)METHANE PHOTOCHEMISTRY. PHOTOCHEMISTRY OF 2-(3,4-PENTADIENYLIDENE)INDAN-1,3-DIONE DERIVATIVES

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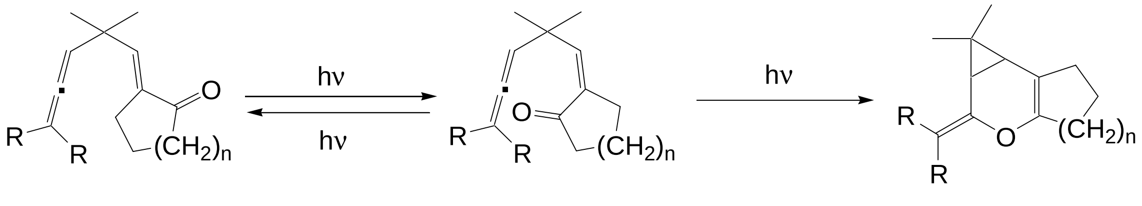
Abstract —— 2-(3,4-Pentadienylidene)indan-1,3-dione derivatives underwent the photochemical intramolecular *oxa*-Diels-Alder reaction to produce pyrans. The *oxa*-Diels-Alder reaction proceeded *via* the singlet-excited state.

INTRODUCTION

We reported the photochemistry of allenyl(vinyl)methanes in which the vinyl moiety is an electron deficient alkene system such as the ylidenemalonate,[1-5] ylidenemalononitrile,[2] yilidene-2,4-pentadione,[7] α,β-unsaturated ester,[1,2,4] and α,β-unsaturated ketone.[7] These compounds underwent various photochemical reactions depending on the multiplicities, substituents, energy levels of the triplet excited-state, or formation of the intramolecular CT complex. We have recently reported that the allenyl(vinyl)methane in which the vinyl moiety is a methylenecyclopentanone system (Scheme 1; n =1) mainly underwent the slow *E-Z* geometrical isomerization and intramolecular *oxa*-Diels-Alder reaction with prolonged irradiation, whereas the intramolecular *oxa*-Diels-Alder reaction of the methylenecyclohexanone analog (Scheme 1; n = 2) hardly occurred.[7] Based on these results, we have defined that pyrans are derived from the photochemical intramolecular *oxa*-Diels-Alder reaction of (*Z*)-enones and the torsion angle about the *s-cis* C=C–C=O single bond must be close to 0°.

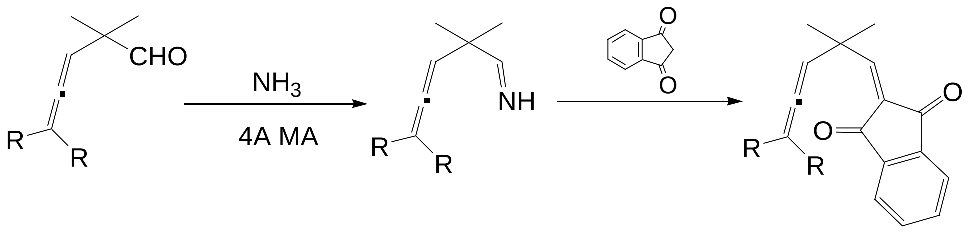


Scheme 1

We have noted the photochemistry of the γ-allenyl-substituted 2-alkylideneindan-1,3-diones (**1** and **2**). Because it is considered that the 2-methyleneindan-1,3-dione system in **1** or **2** is nearly coplanar, **1** and **2** are expected to undergo the photochemical intramolecular *oxa*-Diels-Alder reaction; therefore we are now investigating their photochemistry.

RESULTS AND DISCUSSION

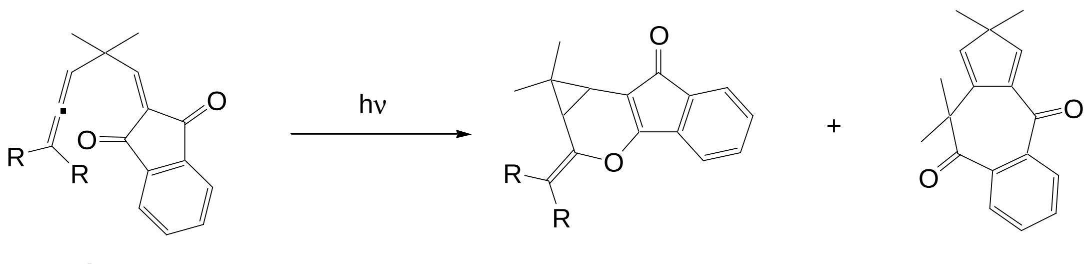
The diketone was prepared as follows.[8] Dry ammonia gas was directly introduced to allenic aldehydes in the presence of 4A molecular sieves to give the allenic imines. A chloroform solution of the imines was added to indan-1,3-dione and the mixture was stirred overnight at room temperature to afford **1** and **2** (Scheme 2).



1: R=H
2: R=Me

Scheme 2

A solution of **1** in benzene under an argon atmosphere was irradiated for 2.5 h using a 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, the residue was chromatographed on silica gel to give a pyran (**3**) as the sole product in 41% isolated yield (Scheme 3). In the ^{13}C-NMR spectrum of **3**, the carbonyl carbon signal was observed at δ 192.3 ppm. In addition, the ^{1}H-NMR spectrum showed doublet peaks (J = 8.4 Hz) at δ 1.83 and 1.87 ppm, respectively, and the IR spectrum showed a carbonyl band at 1702 cm^{-1}. Taking into account the other spectroscopic data and elemental analysis, compound (**3**) was determined to be a pyran.



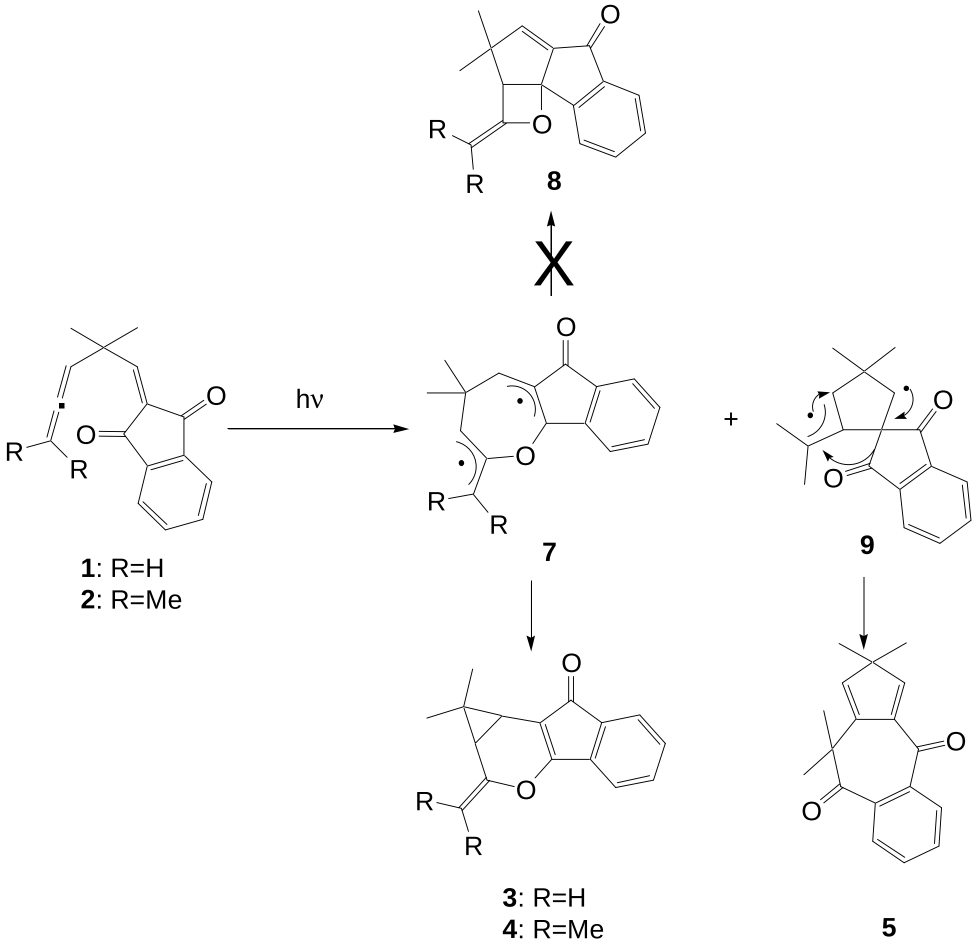
1: R=H
2: R=Me

3: R=H
4: R=Me

5

Scheme 3

On the other hand, during the photolysis of **2**, two photoproducts (**4** and **5)** were isolated by medium-pressure silica gel chromatography in 12% and 13% yields, respectively. The structure of **4** was elucidated on the basis of its NMR, IR, MS spectral data and element analysis. The ^{13}C-NMR spectrum of **5** showed two carbonyl carbons at δ 187.2 and 202.7, and the ^{1}H-NMR spectrum showed cyclopentadienyl protons (δ 6.14 and 7.26 ppm) having a long range coupling constant (*J* = 2.2 Hz).



Scheme 4

In previous papers, we reported that the intramolecular *oxa*-Diels-Alder reaction proceeded as a side-reaction during the photochemistry of allenyl(vinyl)methanes in which one vinyl moiety was a methylene Meldrum's acid system.[5,6] Furthermore, in the photochemistry of the allenyl-substituted alkylidenecycloalkanones, it has been found that the photochemical intramolecular *oxa*-Diels-Alder reaction preferentially occurs in five-membered enones rather than in the six-membered ones. Such differences in the reactivity of the photochemical intramolecular *oxa*-Diels-Alder reaction indicate that the torsion angle and *s-cis* conformation of C=C–C=O are important factors. Because the methylene Meldrum's acid has a boat conformation, its C=C–C=O moiety is kinked.[9] A similar kink of the methylenecyclohexanone system has been demonstrated by the PM3 MO calculation.[7] However, by the PM3 MO method, the torsion angles of the *s-cis* C=C–C=O moieties of **1** and **2** were calculated as 1.9°

and 1.4°, respectively; hence **1** and **2** have the conformations which easily undergo the photochemical intramolecular *oxa*-Diels-Alder reaction. The *oxa*-Diels-Alder reaction of **1** was unquenchable with 2-methyl-1,3-butadiene (concn. ~ 4.77 mol dm^{-3}). Therefore, oxygen in the excited singlet state of the carbonyl group in **1** or **2** electrophilically attacks the center carbon of the allene to afford a biradical (**7**) and then the ring closure of **7** leads to the pyran (**3** or **4**) (Scheme 4). The initial pathway in this reaction parallels the Paternó-Büchi reaction[10] of ketones with alkenes, dienes, or allenes,[10b,11] though the resulting biradical (**7**) prefers the pathway for the formation of **3** or **4** to that of an oxetane (**8**).[12,13] From the yields of the pyrans (**3** and **4**), it seems that the indan (**1**) is more susceptible to the intramolecular *oxa*-Diels-Alder reaction than **2**. This is considered as follows. The center carbon of the allene has two π-orbitals, and the HOMO of the 1,2-propadienyl group in **1** lies at the C_1-C_2 moiety, while that of the 3-methyl-1,2-butadienyl group in **2** is the C_2-C_3 moiety.[5] Therefore, **1** undergoes the intramolecular *oxa*-Diles-Alder reaction due to a favorable MO interaction between oxygen of the carbonyl group and center carbon of the 1,2-propadienyl group.[5] In the case of **2**, two interactions competitively takes place, i.e., the interaction for the *oxa*-Diels-Alder reaction and the interaction between the π-orbitals of the C_2 on the C_2-C_3 of the 3-methyl-1,2-butadienyl and the α-carbon. The later interaction is responsible for the production of a cyclopenta-1,3-dienyl radical (**9**). The acyl migration of **9** led to **5** (Scheme 4).

In conclusion, the indans (**1** and **2**) have a coplanar *s-cis* enone moiety, and undergo the intramolecular *oxa*-Diels-Alder reaction. This reaction initially bonds between the allene center carbon and oxygen of the excited carbonyl and the ring closure of the resulting diallyl radical (**7**) produces the pyrans (**3** and **4**).

EXPERIMENTAL

General

The melting points were determined on a micro hot stage (Yazawa) and are uncorrected. The NMR spectra were measured in a $CDCl_3$ or C_6D_6 solution using Bruker Avance-400 and JEOL JNM-EX 90 spectrometers. The IR spectra were obtained using a BIO-RAD FTS-60A spectrophotometer. The MS and HRMS were obtained using a JEOL JMS AX-500 spectrometer.

2-(2,2-Dimethyl-3,4-pentadienylidene)indan-1,3-dione (1).

The method for the condensation of the imine with carbonyl compounds described by Bihlmayer *et al.* was used.[8] Ammonia gas was introduced into a mixture of 2,2-dimethyl-3,4-pentadien-1-al[5] (5.51 g, 50 mmol) and molecular sieves 4A (5 g) in a test tube for 1 h at rt. The reaction mixture was filtered to give 2,2-dimethyl-3,4-pentadienylideneamine: ^1H NMR (90 MHz, $CDCl_3$) δ 1.20 (6H, s, Me x 2), 4.6 - 5.3 (3H, m), and 7.51 (1H, s). This compound was used for the following reaction. The imine was dissolved in chloroform (50 mL). To the solution was added this solution of indan-1,3-dione (6.90 g, 50 mmol) in chloroform (50 mL) and the mixture was stirred for 24 h at rt. After evaporation of the solvent, the residue was subjected to silica gel chromatography using EtOAc/hexane (1:9, *v/v*) as the eluent to give **1** (1.27, 13%) as orange crystals: mp 65 - 66 °C (hexane/chloroform); IR (neat) 1951 (C=C=C), 1735 (C=O), 1690 (CO), and 1631 (C=C) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.51 (6H, s, 2-Me X 2), 4.84 (2H, dd, *J* = 6.6 and 7.1 Hz, CH_2=C=C), 5.79 (1H, dd, *J* = 6.6 and 7.1 Hz, CH=C=C), 7.41 (1H, s, CH=C), and 7.75 – 8.03 (4H, m, ArH); ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 28.0 (2C, q, 2-Me), 37.0 (s, 2-C), 78.0 (t, 5-C), 98.5 (d, 3-C) 123.4 (d), 123.5 (d), 131.0 (s), 135.3 (d), 135.5 (d), 140.2 (s), 142.6 (s), 160.7 (d, 1-C), 188.6 (s, C=O), 189.4 (s, C=O), and 206.9 (s, 4-C); MS *m/z* (rel intensity) 238 (M^+, 27), 224 (16), 223 (100), 200 (10), 195 (15), 167 (10), 165 (14), 152 (16), 128 (10), 105 (15), 78 (24), 77 (17), 76 (12), and 43 (10). HRMS Found: *m/z* 238.0973. Calcd for $C_{16}H_{14}O_2$: 238.0994. *Anal.* Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.80; H, 5.86.

2-(2,2,5-Trimethyl-3,4-hexadienylidene)indan-1,3-dione (2).

In a similar manner as that described above, the reaction of 2,2,5-trimethyl-3,4-hexadien-1-al[5] (13.8 g, 0.10 mol) with ammonia gas gave 2,2,5-trimethyl-3,4-hexadienylideneamine: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.14 (3H, s, Me), 1.16 (3H, s, Me), 1.68 (6H, *J* = 3.0 Hz, C=C=CMe_2), 5.00 (1H, septet, *J* = 3.0 Hz, CH=C=C), and 7.49 (1H, s, C=NH). To the solution of the imine in $CHCl_3$ (50 mL) was added indan-1,3-dione (10.59 g, 70 mmol) and then the mixture was stirred for 24 h. The reaction mixture was evaporated in vacuo and the residual oil was chromatographed on silica gel using 10% EtOAc/hexane to give **2** (3.92 g, 37%) as an orange viscous oil; IR (neat) 1966 (C=C=C), 1735 (C=O), 1697 (C=O), and 1632 cm^{-1}(C=C); ^{1}H-NMR (90 MHz, $CDCl_3$) δ 1.48 (6H, s, 2-Me X 2), 1.69 (6H, d, *J* = 2.6 Hz, C=C=CMe_2), 5.50 (1H, septet, *J* = 2.6 Hz, CH=C=C), 7.43 (1H, s, CH=C), and 7.74 – 8.04 (4H, m, ArH); ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 20.6 (2C, q, 6-C), 28.1 (2C, q, 2-Me), 38.3 (s, 2-C), 97.6 (d, 3-C), 98.6 (s, 5-C), 123.2 (d), 123.4 (d), 130.8 (s), 135.1 (d), 135.3 (d), 140.1 (s), 142.6 (s), 161.5 (d, 1-C), 188.4 (s, C=O), 189.4 (s, C=O), and 200.1 (s, 4-C); MS *m/z* (rel intensity) 266 (M^+, 95), 252 (19), 233 (10), 223 (21), 211 (12), 209 (11), 208 (10), 200 (10), 199 (12), 197 (11), 165 (10), 159 (15), 152 (11), 133 (10), 128 (13), 115 (12), 105 (28), 83 (14), 77 (21), 76 (11), 67 (14), 65 (10), 44 (10), and 43 (16). HRMS Found: *m/z* 266.1365. Calcd for $C_{18}H_{18}O_2$: 266.1307.

Photoreaction of 1

A solution of **1** (937 mg, 4.00 mmol) in benzene (400 mL) was irradiated for 2.5 h using a 100-W high-pressure mercury lamp with a Pyrex jacket under an argon atmosphere at rt. After evaporation of the solvent, the residue was subjected to medium-pressure silica gel chromatography using 10% ether-hexane as the eluent to give 5,6-benzo-10,10-dimethyl-7-methylene-3-oxatricyclo[7.1.0.$0^{4,8}$]-deca-4(8)-en-7-one (**3**) in 41% (386 mg) yield as orange crystals: mp 82-85 °C (hexane); IR (KBr) 1702 (C=O), 1654 (C=C), and 1594 (C=C) cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, s, 10-Me), 1.26 (3H, s, 10-Me), 1.83 (1H, d, *J* = 8.4 Hz), 1.87 (1H, d, *J* = 8.4 Hz), 4.65 (1H, d, *J* = 1.6 Hz, =CH), 5.00 (1H, d, *J* =1.6 Hz, =CH), 7.13 (1H, d, *J* = 6.7 Hz, ArH), 7.22 –7.32 (2H, m, ArH), and 7.39 – 7.41 (1H, m, ArH); ^{13}C-NMR (100MHz, $CDCl_3$) δ 15.4 (q), 19.0 (q), 25.2 (d), 26.2 (d), 27.4 (s), 96.1 (t), 107.4 (s), 117.7 (d), 121.3 (d), 129.8 (d), 132.1 (d), 132.9 (s), 137.1 (s), 153.0 (s), 168.4 (s), and 192.3 (s); MS *m/z* (rel intensity) 238 (M^+, 76), 224 (17), 223 (100), 196 (10), 195 (15), 165 (14), 152 (15), 105 (16), 77 (11), and 76 (11). HRMS Found: *m/z* 238.0966. Calcd for $C_{16}H_{14}O_2$: 238.0994. *Anal.* Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.75; H, 5.84.

Photoreaction of 2

In a manner similar to that described above for the photoreaction, a solution of **2** (1.07 g, 4.00 mmol) in benzene (400 mL) was irradiated to give **4** (126 mg, 12%) and **5** (132 mg, 13%).

5,6-Benzo-2-isopropyridene-10,10-dimethyl-3-oxatricyclo[7.1.0.0^{4,8}]dec-4(8)-en-7-one (**4**): orange crystals; mp 115 – 116 °C (hexane/chloroform); IR (KBr) 1695, 1636, and 1594 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 0.77 (3H, s, 10-Me), 1.27 (3H, s, 10-Me), 1.72 (2H, s, 1- and 9-CH), 1.80 (3H, s, =CMe), 1.90(3H, s, =CMe), and 7.14 – 7.45 (4H, m, ArH); ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ 15.7 (q), 16.7 (q), 18.3 (d), 18.9 (q), 21.5 (d), 26.0 (q), 26.9 (s), 106.0 (s), 116.2 (s), 117.4 (d), 121.0 (d), 130.0 (d), 131.7 (d), 133.2 (s), 137.4 (s), 140.5 (s), 169.1 (s), and 192.5 (s); MS *m/z* (rel intensity) 266 (M^+, 97), 265 (10), 253 (19) 252 (100), 223 (17), 209 (12), 165 (10), 152 (10), 105 (21), 77 (14), and 41 (14). HRMS Found: *m/z* 266.1346. Calcd for $C_{18}H_{18}O_2$: 266.1307. *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.20; H, 6.77.

3,4-Benzo-6,6,9,9-tetramethylbicyclo[5.3.0]deca-1(10),7-dien-2,5-dione (**5**): a red viscous oil; IR (KBr) 1739, 1687, 1650, and 1590 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 1.23 (6H, s, 9-Me X 2), 1.43 (6H, s, 6-Me X 2), 6.14 (1H, d, *J* = 2.2 Hz, 8-CH), 7.26 (1H, d, *J* = 2.2 Hz, 10-CH), 7.60 – 7.84 (3H, m, ArH), and 8.32 – 8.36 (1H, m, ArH); ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ 21.7 (2C, q), 25.0 (2C, q), 49.4 (s), 51.1 (s), 129.7 (d), 130.5 (d), 131.8 (d), 133.4 (d), 134.1 (s), 137.5 (s), 139.6 (s), 141.4 (d), 142.1 (s), 158.4 (d), 187.2 (s), and 202.7 (s); MS *m/z* (rel intensity) 266 (M^+, 81), 252 (19), 251 (100), 225 (11), 224 (11), 223 (21), 211 (34), 209 (10), 208 (13), 165 (13), 133 (17), 105 (13), 77 (12), 44 (12), and 43 (16). HRMS Found: *m/z* 266.1307. Calcd for $C_{18}H_{18}O_2$: 266.1307.

Quenching Effect

A benzene solution (10 mL) of **1** (5.00 mmol dm^{-3}) and 2-methyl-1,3-butadiene (0 – 4.77 mol dm^{-3}) in a test tube was degassed with nitrogen and then irradiated with a 100-W high-pressure mercury lamp through a Pyrex filter. The irradiation was stopped within 25% of the conversation of **1**. After evaporation of the solvent, the residual oil was analyzed by ^{1}H-NMR (400 MHz) and the ratio of **1** and **3** was determined.

MO Calculation

The MO calculations were performed using the PM3 method of Mac Spartan Plus of Wavefunction, Inc.

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