[2+2] Photocycloaddition Reaction of 5-Arylfuran-2,3-diones to Trimethylsilyloxyethylenes

Takehiro SANO,*[a] Nobuyuki KOSEKI,[a] Toshiaki SAITOH,[a] Yoshie HORIGUCHI,[a] Jun TODA,[a] Fumiyuki KIUCHI,[b] and Yoshisuke TSUDA[b]

Showa College of Pharmaceutical Sciences,[a] 3–3165 Higashi-tamagawagakuen, Machida-shi, Tokyo 194, Japan and Faculty of Pharmaceutical Sciences, Kanazawa University,[b] 13–1 Takara-machi, Kanazawa 920, Japan.

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The photocycloaddition reaction of 5-phenylfuran-2,3-dione (1a) to 2-trimethylsilyloxybutadiene proceeded in a [2s+2s] manner with high regio- and stereo-selectivities to give a 2-oxabicyclo[3.2.0]heptane-3,4-dione 2 with 7-*endo*-OTMS-7-*exo*-vinyl stereochemistry. 5-Arylfuran-2,3-diones (1a—e) on similar photocycloaddition with 1-phenyl-1-trimethylsilyloxyethylene gave the corresponding 7-aryl derivatives 3a—e with the same regio- and stereo-chemistries in good yields. This stereochemical result of *O-endo* selectivity is consistent with the prediction obtained from the stereo-selection rule proposed for the enone-olefin photocycloaddition reaction. The reaction provides an efficient method for the synthesis of poly-functionalized cyclobutane derivatives.

Key words [2+2] photocycloaddition; dioxofuran; cyclobutane; stereochemistry; trimethylsilyloxyethylene

The [2+2] photocycloaddition reaction of 1*H*-pyrrole-2,3-dione (dioxopyrroline) to olefins has been effectively utilized for construction of hydroindole,[1] erythrinane,[2] and azatropolone.[3] In addition to these synthetic studies, we have proposed an experimental rule regarding the factors controlling the stereochemical pathway of enone-olefin photocycloaddition.[4] This rule seems to work reliably for rationalizing the stereochemical results, in particular, in the photocycloaddition reaction of dioxopyrroline-olefin pairs.[5] The examples hitherto presented indicate that the polarity (the magnitude of donor–acceptor interaction) of the pair in the excited π-complex plays an important role in determining the stereochemical pathway of the reaction. The donor–acceptor interaction could be evaluated not only in terms of the electronic properties of the addends,[5a–c] but also in terms of their steric relationship.[5e,f]

In this paper we describe the photocycloaddition reaction of 5-arylfuran-2,3-diones (**1**, 5-Ar-dioxofurans; "*O*-analogs of dioxopyrroline") to trimethylsilyloxyethylenes, providing further examples to show that the stereoselection rule works reliably for predicting the stereochemical results of [2+2] photocycloaddition reaction.

Results and Discussion

Irradiation of a solution of the 5-Ar-dioxofuran **1a** and 2-trimethylsilyloxybutadiene in dimethoxyethane (DME) with $\lambda > 300$ nm light for 25 min at 0 °C gave a cyclobutane **2** in 99% yield. The product **2** has the molecular formula $C_{17}H_{20}O_4Si$, indicating that the product is a 1 : 1 adduct of the addends. The adduct **2** exhibited strong carbonyl absorption (1795 cm^{-1}) due to a 5-membered ketone and a γ-lactone in the IR spectrum. The presence of a ketone group in **2** was confirmed by the ^{13}C-NMR signal at δ 193.7 ppm. In addition to these data, the observation of signals due to four sp^3 carbons in the ^{13}C-NMR spectra [δ 34.4, 42.3, 84.0, 87.2 ppm] indicated that **2** has a cyclobutane structure. Furthermore, the presence of ABX signals attributable to the cyclobutane protons at δ 2.25, 2.95, and 3.39 ppm clearly indicated that **2** is an adduct

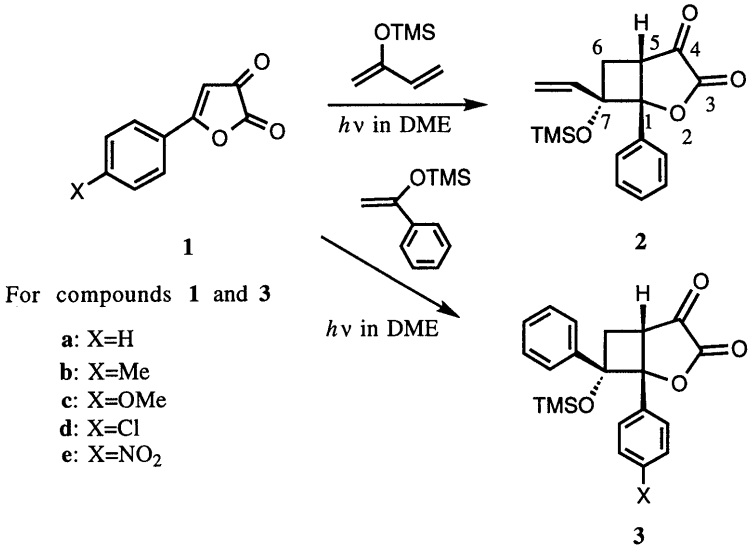

Chart 1

* To whom correspondence should be addressed.

with a head-to-tail (H-T) regiochemistry.

Similarly, 1-phenyl-1-trimethylsilyloxyethylene, on photo-reaction with **1a**, gave a cyclobutane **3a** in 75% yield. The ^{1}H-NMR signals due to three protons on the cyclobutane ring appeared as extremely complex multiplets when the spectrum was measured with a 90 MHz machine, while the signals obtained with a 500 MHz machine were simple multiplets. Analysis of the signals by using appropriate software[6] indicated that the signal pattern is consistent with an ABB′ system [δ 2.70 (A), 3.50 (B), and 3.54 ppm (B′)] with the coupling constants of $J'_{AB}=10$ Hz, $J_{AB}=0$ Hz, and $J'_{BB}=10$ Hz, thus confirming the H-T regiochemistry.

The stereochemistry of C-7 substituents of **2** and **3a** was elucidated by chemical means. Acidic treatment of **2** with 5% HCl in tetrahydrofuran (THF) caused a skeletal rearrangement to give a 5,6-dihydro-2-pyrone derivative **4a** in 90% yield. A similar acidic treatment of **3a** also produced a dihydropyrone **4b** in 74% yield. The products **4a** and **4b** showed similar spectral characteristics. The assigned structures were well consistent with the spectral data; for example, those of **4a** indicated the presence of a benzoyl (IR: 1680 cm^{-1} and ^{13}C-NMR δ: 197.1 ppm), a lactone carbonyl (IR: 1725 cm^{-1} and ^{13}C-NMR δ: 162.6 ppm), a trisubstituted double bond [^{1}H-NMR δ: 5.83 and ^{13}C-NMR: 129.0 (d), 137.8 (s) ppm], and a methylene [^{1}H-NMR δ: 2.75, 3.43, and ^{13}C-NMR: 31.1 (t) ppm]. The presence of an enol moiety was proved by acetylation of **4a** and **4b** to afford the corresponding enol acetates **5a** and **5b** in 85% and 74% yields, respectively.

Formation of **4** can be rationalized as follows (Chart 2): The reaction should proceed *via* an alcohol **6** formed by desilylation. In fact, the alcohol **6a** was isolated from an Et_2O solution of **2** which had been allowed to stand at room temperature for two weeks. The hydroxyl group at C-7 attacks the lactone carbonyl to yield an ortho-ester **7**. This then undergoes a ring-opening reaction of the furan with simultaneous cleavage of the cyclobutane ring to yield the dihydropyrone **4**. The participation of 7-OH should be the driving force for this skeletal rearrangement, which is possible only when the intermediate **6** has a *cis*-fused ring junction (at C-1 and C-5) and an *endo* 7-OH group, thus suggesting that the adducts **2** and **3** was are the 7-*endo* trimethylsilyloxy (OTMS) and the 7-*exo* vinyl (phenyl) derivatives with a *cis*-fused ring junction.

Next, we carried out the photocycloaddition of 5-Ar-dioxofurans with a methyl (**1b**), methoxy (**1c**), chloro (**1d**), or nitro (**1e**) substituent at the *para*-position of the 5-phenyl group in order to investigate whether these substituents affect the stereochemical pathway of this reaction. Photocycloaddition of **1b—e** to 1-phenyl-1-trimethylsilyloxyethylene proceeded in the same manner to give the cyclobutanes **3b—e** as sole adducts in moderate to good yields, respectively (Table 1). The similarity of their ^{1}H-NMR and ^{13}C-NMR spectra to that of **3a** confirmed not only the regiochemistry, but also the stereochemistry of **3b—e** as 7-*endo* OTMS-7-*exo* Ar, so that the adduct with the same stereochemistry was obtained regardless of the electronic nature of the aryl group. Finally, the structure and stereochemistry of the adducts were established by X-ray crystallographic analysis of **3e** (Fig. 1).

The formation of the OTMS-*endo*-isomers **2** and **3** is a result of [2s+2s] addition from a *O-endo*-π-transition state **8**, as shown in Chart 3. This stereochemical result is similar to that in the transformation of the dioxopyrroline **9** to 2-trimethylsilyloxybutadiene and to 1-phenyl-1-trimethylsilyloxyethylene.[5a] This observed *endo*-selectivity, just as in the case of **9**, is consistent with the prediction obtained from the stereoselection rule,[4] which states that the addition, when the pair is very polar, proceeds in

Table 1. Photocycloaddition of 5-Ar-dioxofurans **1a—f** with 1-Vinyl- or 1-Phenyl-1-trimethylsilyloxyethylenes

Dioxofuran **1** (X)	Olefin	Adduct	Yield (%)
1a (H)	1-Vinyl	**2a**	99
1a (H)	1-Phenyl	**3a**	75
1b (Me)	1-Phenyl	**3b**	47
1c (OMe)	1-Phenyl	**3c**	40
1d (Cl)	1-Phenyl	**3d**	67
1e (NO_2)	1-Phenyl	**3e**	67

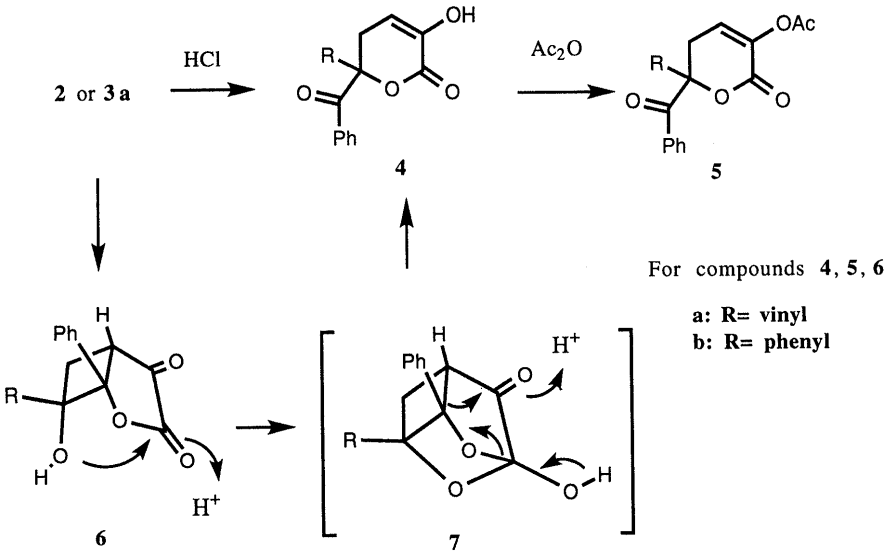

Chart 2

a [2s+2s] manner *via* a favored *endo*-π-complex. The double bond of the dioxofuran ring, which acts as an ene-acceptor, is anticipated to be more electron-deficient than that of the dioxopyrroline ring, since oxygen is more electronegative than nitrogen is. Consequently, the magnitude of the polarity of the dioxofuran–olefin pair should be larger than that of the dioxopyrroline–olefin pair. Clearly, the dioxofuran–trimethylsilyloxyethylene pair can be assigned as very polar, considering that the corresponding dioxopyrroline pair is very polar.[4]

In conclusion, this is a first example demonstrating that dioxofuran is an excellent ene-acceptor in photocycloaddition, and the reaction provides an efficient and simple method for the synthesis of poly-functionalized cyclobutane derivatives.

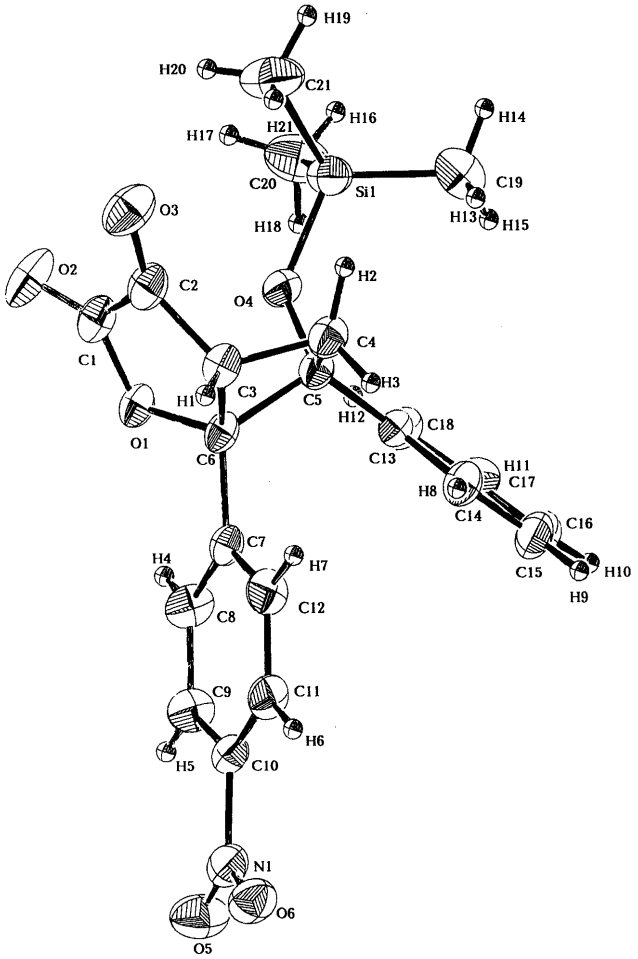

Fig. 1. Stereo-Structure of Photo-Adduct **3e**

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagimoto micro hot-stage melting point apparatus and are uncorrected. IR spectra were taken in Nujol mulls for solids and CH_2Cl_2 solution for gums with a Hitachi 260-10 spectrometer and are given in cm^{-1}. UV spectra were recorded in dioxane solution with a Hitachi 200-10 spectrometer and are given in λ_{max} nm (ε). ^{1}H-NMR (90 MHz) and ^{13}C-NMR (25.0 MHz) spectra were taken in $CDCl_3$ solution with tetramethylsilane as an internal standard on a JEOL FX-100 spectrometer. High-resolution mass spectra (HR-MS) were recorded on a JEOL JMS-D300 mass spectrometer. Elemental analysis was performed with a Yanaco CHN CORDER MT-3. For column chromatography, silica gel (Mallinkrodt, CC-7) was used. Thin-layer chromatography (TLC) was performed on Merck precoated Silica gel $60F_{254}$ plates. Medium-pressure liquid chromatography (MPLC) was performed on a Kusano CIG prepacked silica gel column. The photolysis was done by internal irradiation using a 300 W high-pressure mercury lamp (Eikosha Halos PIH 300) with a Pyrex filter. 5-Ar-dioxofurans (**1a—e**) were prepared according to the known procedure.[7]

Photocycloaddition of 1a with Trimethylsilyloxyethylenes (General Procedure) A solution of **1** (2.0 g, 11.5 mmol) and an olefin (2 molar eq) in DME (300 ml) was irradiated at 0 °C for 25 min. After removal of the solvent *in vacuo*, the residue in benzene was chromatographed. Elution with CH_2Cl_2–benzene (1 : 1) gave the cyclobutanes **2** and **3**, which were separated by MPLC using AcOEt–hexane (1 : 1) and fractional crystallizations from AcOEt–hexane–benzene.

(1*R**,5*S**,7*S**)-1-Phenyl-7-trimethylsilyloxy-7-vinyl-2-oxabicyclo-[3.2.0]heptane-3,4-dione (**2**): 3.6 g (99%). Colorless prisms, mp 70—72 °C. IR: 1795. ^{1}H-NMR: 0.13 (9H, s, OTMS), 2.25 (1H, dd, J=2, 12 Hz, H-6), 2.95 (1H, dd, J=9, 12 Hz, H-6), 3.39 (1H, dd, J=2, 9 Hz, H-5), 5.05 (1H, br d, J=1, 18 Hz, CH=C$\underline{H}_2$), 5.07 (1H, br d, J=10 Hz, CH=C$\underline{H}_2$), 5.60 (1H, dd, J=10, 18 Hz, C$\underline{H}$=CH$_2$), 7.26—7.38 (5H, m, ArH). ^{13}C-NMR: 1.64 (q × 3, OTMS), 34.4 (t, C-6), 42.3 (d, C-5), 84.0 (s, C-7 or C-1), 87.2 (s, C-1 or C-7), 118.1 (t, CH=$\underline{C}$H$_2$), 125.6 (d × 2, Ph), 128.6 (d × 2, Ph), 128.9 (d, Ph), 133.6 (s, Ph), 136.4 (d, $\underline{C}$H=CH$_2$), 161.2 (s, C-3), 193.7 (s, C-4). HR-MS *m/z*: 316.1118 (Calcd for

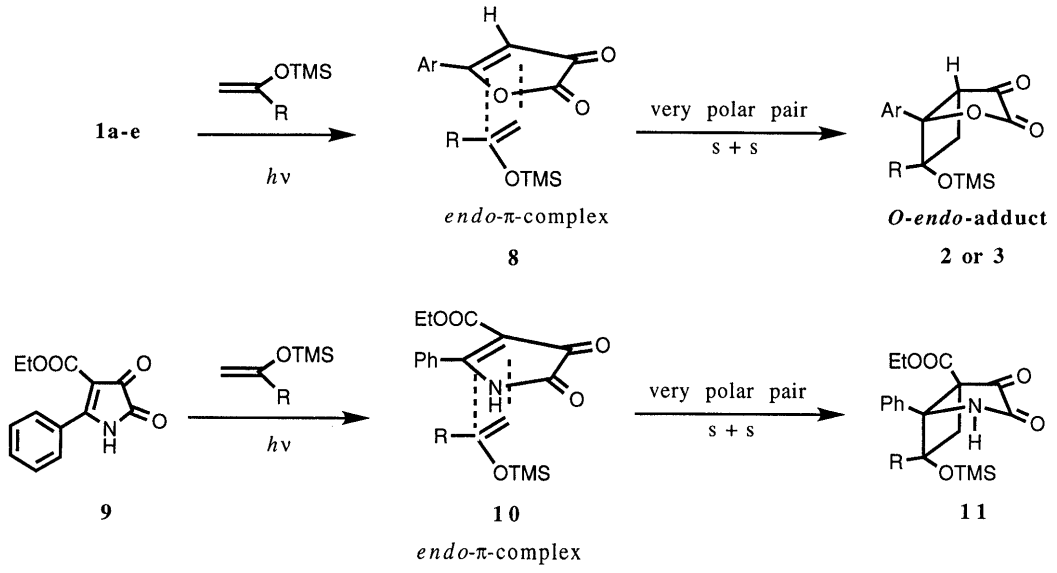

Chart 3

$C_{17}H_{20}O_4Si$ (M^+): 316.1128).

An ethereal solution of **2** (300 mg) was allowed to stand for 2 weeks at room temperature. After evaporation of the solvent, the residue was recrystallized from AcOEt–Et_2O–hexane to give (1*R**,5*R**,7*R**)-7-hydroxy-1-phenyl-7-vinyl-2-oxabicyclo[3.2.0]heptane-3,4-dione (**6a**) (190 mg, 82%), colorless prisms, mp 86—88 °C. IR: 3500, 3200, 1765. ^{1}H-NMR ($CDCl_3$–DMSO-d_6): 2.25 (1H, dd, J=3, 13 Hz, H-6), 2.73 (1H, dd, J=10, 13 Hz, H-6), 3.52 (1H, dd, J=3, 10 Hz, H-5), 4.99 (1H, dd, J=2, 10 Hz, CH=C$\underline{H}_2$), 5.20 (1H, dd, J=2, 17 Hz, CH=C$\underline{H}_2$), 5.50 (1H, dd, J=10, 17 Hz, C$\underline{H}$=CH$_2$), 7.3—7.4 (5H, m, ArH). HR-MS m/z: 244.0760 (Calcd for $C_{14}H_{12}O_4$ (M^+): 244.0735).

(1*R**,5*S**,7*S**)-1,7-Diphenyl-7-trimethylsilyloxy-2-oxabicyclo[3.2.0]-heptane-3,4-dione (**3a**): 3.16 g (75%). Colorless needles, mp 164—166 °C. IR: 1790, 1765. ^{1}H-NMR (270 MHz): 0.13 (9H, s, OTMS), 2.6—2.8 (1H, m, H-6), 3.4—3.6 (2H, m, H-5, 6), 7.1—7.5 (10H, m, ArH). ^{13}C-NMR: 1.01 (q×3, OTMS), 35.6 (t, C-6), 43.7 (d, C-5), 86.4 (s, C-7 or C-1), 87.3 (s, C-1 or C-7), 125.1 (d×2, Ph), 127.0 (d×2, Ph), 127.9 (d, Ph), 128.2 (d×2, Ph), 134.1 (s, Ph), 137.8 (s, Ph), 161.6 (s, C-3), 193.7 (s, C-4). HR-MS m/z: 366.1317 (Calcd for $C_{21}H_{22}O_4Si$ (M^+): 366.1287).

(1*R**,5*S**,7*S**)-7-Phenyl-1-(*p*-tolyl)-7-trimethylsilyloxy-2-oxabicyclo-[3.2.0]heptane-3,4-dione (**3b**): Yield, 1.653 g (47%). Colorless prisms from CH_2Cl_2, mp 139—141 °C. IR: 1796, 1773. ^{1}H-NMR: 0.04 (9H, s, OTMS), 2.39 (3H, s, Me), 2.6—2.9 (1H, m, H-6), 3.4—3.7 (2H, m, H-5, 6), 7.2—7.4 (9H, m, Ph). ^{13}C-NMR: 1.1 (q×3, OTMS), 21.0 (q, Me), 35.0 (t, C-6), 44.0 (d, C-5), 86.4 (s, C-7 or C-1), 87.3 (s, C-1 or C-7), 125.0 (d×2, Ar), 127.1 (d×2, Ar), 128.0 (d×2, Ar), 128.3 (d, Ar), 129.0 (d×2, Ar), 131.2 (s, Ar), 138.0 (s, Ar), 138.2 (s, Ar), 161.8 (s, C-3), 194.6 (s, C-4). HR-MS m/z: 380.1474 (Calcd for $C_{22}H_{24}O_4Si$ (M^+): 380.1444).

(1*R**,5*S**,7*S**)-1-(4-Methoxyphenyl)-7-phenyl-7-trimethylsilyloxy-2-oxabicyclo[3.2.0]heptane-3,4-dione (**3c**): Yield, 1.552 g (40%). Colorless needles from CH_2Cl_2, mp 131.5—132 °C. IR: 1792, 1775. ^{1}H-NMR: 0.14 (9H, s, OTMS), 2.5—2.8 (1H, m, H-6), 3.3—3.6 (2H, m, H-5, 6), 3.84 (3H,s, OMe), 6.8—7.4 (9H, m, Ph). ^{13}C-NMR: 1.0 (q×3, OTMS), 35.2 (t, C-6), 43.6 (d, C-5), 55.0 (q, OMe), 86.4 (s, C-7 or C-1), 87.2 (s, C-1 or C-7), 113.6 (d×2, Ar), 126.0 (s, Ar), 126.5 (d×2, Ar), 126.9 (d×2, Ar), 127.9 (d×2, Ar), 128.2 (d, Ar), 138.0 (s, Ar), 159.3 (s, Ar), 161.7 (s, C-3), 193.8 (s, C-4). CI-MS m/z: 397 (MH^+).

(1*R**,5*S**,7*S**)-1-(4-Chlorophenyl)-7-phenyl-7-trimethylsilyloxy-2-oxabicyclo[3.2.0]heptane-3,4-dione (**3d**): Yield, 2.600 g (67%). Colorless prisms from CH_2Cl_2, mp 181—182 °C. IR: 1802, 1771. ^{1}H-NMR: 0.04 (9H, s, OTMS), 2.6—2.9 (1H, m, H-6), 3.4—3.7 (2H, m, H-5, 6), 7.2—7.5 (9H, m, Ph). ^{13}C-NMR: 1.0 (q×3, OTMS), 34.5 (t, C-6), 42.8 (d, C-5), 85.4 (s, C-7 or C-1), 85.9 (s, C-1 or C-7), 125.5 (d×2, Ph), 125.9 (d×2, Ph), 127.2 (d×2, Ph), 127.5 (d×3, Ph), 131.8 (s, Ph), 133.3 (s, Ph), 136.6 (s, Ph), 160.3 (s, C-3), 192.3 (s, C-4). HR-MS m/z: 400.0892 (Calcd for $C_{21}H_{21}ClO_4Si$ (M^+): 400.0895).

(1*R**,5*S**,7*S**)-1-(4-Nitrophenyl)-7-phenyl-7-trimethylsilyloxy-2-oxabicyclo[3.2.0]heptane-3,4-dione (**3e**): Yield, 2.525 g (67%). Colorless prisms from CH_2Cl_2, mp 195—197 °C. IR: 1792, 1775, 1607, 1516. ^{1}H-NMR: 0.13 (9H, s, OTMS), 2.5—2.9 (1H, m, H-6), 3.4—3.9 (2H, m, H-5, 6), 7.1—7.4 (5H, m, Ar), 7.5—7.9 (2H, m, Ar), 8.1—8.3 (2H, m, Ar). ^{13}C-NMR: 1.0 (q×3, OTMS), 35.8 (t, C-6), 43.8 (d, C-5), 84.2 (s, C-7 or C-1), 86.6 (s, C-1 or C-7), 123.5 (d×2, Ar), 126.1 (d×2, Ar), 126.9 (d×2, Ar), 128.4 (d×2, Ar), 128.9 (d, Ar), 137.2 (s, Ar), 141.6 (s, Ar), 147.5 (s, Ar), 160.7 (s, C-3), 192.6 (s, C-4). HR-MS m/z: 411.1145 (Calcd for $C_{21}H_{21}NO_6Si$ (M^+): 411.1138).

Skeletal Rearrangement of Photoadducts 2 and 3a with Hydrochloric Acid A solution of the adduct (**2**, 100 mg or **3a**: 300 mg) in THF (20 ml) and 5% HCl (20 ml) was stirred at room temperature for 1.5 h. The mixture was diluted with CH_2Cl_2 and the organic layer was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and evaporated *in vacuo* to dryness. The residue in CH_2Cl_2 was chromatographed over Florisil to give the dihydropyrone **4** (**4a**, 77 mg, 90%; **4b**, 177 mg, 74%).

6-Benzoyl-3-hydroxy-6-vinyl-5,6-dihydro-2*H*-pyran-2-one (**4a**): Colorless gum. IR: 3440, 1725, 1680, 1600, 1580. UV: 251 (10900). ^{1}H-NMR: 2.75 (1H, dd, J=3, 18 Hz, H-5), 3.43 (1H, dd, J=6, 18 Hz, H-5), 5.43 (1H, d, J=11 Hz, CH=C$\underline{H}_2$), 5.59 (1H, d, J=17 Hz, CH=C$\underline{H}_2$), 5.83 (1H, dd, J=3, 6 Hz, H-4), 6.16 (1H, dd, J=11, 17 Hz, C$\underline{H}$=CH$_2$), 7.3—7.6 (3H, m, ArH), 8.0—8.1 (2H, m, ArH). ^{13}C-NMR: 31.1 (t, C-5), 91.0 (s, C-6), 110.1 (d, C-4), 118.1 (t, CH=C$\underline{H}_2$) 128.4 (d×2, Ph), 130.0 (d×2, Ph), 133.4 (d, C$\underline{H}$=CH$_2$), 134.2 (d, Ph), 135.4 (s, Ph), 139.7 (s, C-3), 162.6 (s, C-2), 197.1 (s, PhC$\underline{O}$). HR-MS m/z: 244.0724 (Calcd for $C_{14}H_{12}O_4$ (M^+): 244.0734).

6-Benzoyl-3-hydroxy-6-phenyl-5,6-dihydro-2*H*-pyran-2-one (**4b**): Colorless needles from hexane–Et_2O, mp 104—106 °C. IR: 3450, 1710, 1690, 1600, 1580. UV: 252 (15000). ^{1}H-NMR: 2.87 (1H, dd, J=3, 18 Hz, H-5), 3.67 (1H, dd, J=6, 18 Hz, H-5), 5.47 (1H, br s, O$\underline{H}$), 5.91 (1H, dd, J=3, 6 Hz, H-4), 7.3—7.6 (8H, m, ArH), 7.8—7.9 (2H, m, ArH). ^{13}C-NMR: 33.2 (t, C-5), 91.5 (s, C-6), 111.1 (d, C-4), 124.4 (d×2, Ph), 128.3 (d×2, Ph), 128.8 (d, Ph), 129.1 (d×2, Ph), 130.2 (d×2, Ph), 133.2 (d, Ph), 134.0 (s, Ph), 137.6 (s, Ph), 139.7 (s, C-3), 162.6 (s, C-2), 196.6 (s, PhC$\underline{O}$). LRMS m/z: 251 (M^+ −43), 105 (base peak). *Anal.* Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.35; H, 5.08.

Acetylation of 4a and 4b with Acetic Anhydride A solution of **4** (**4a**, 70 mg or **4b**, 100 mg) in pyridine (2 ml) and acetic anhydride (1 ml) was stirred at room temperature for 12 h. The mixture was diluted with CH_2Cl_2 and the organic layer was washed with 5% HCl, 10% $NaHCO_3$, and water, dried over Na_2SO_4, and evaporated *in vacuo* to dryness. The residue in CH_2Cl_2 was passed through a short column of Florisil to give the acetate **5** (**5a**, 70 mg, 85% and **5b**, 85 mg, 74%).

3-Acetoxy-6-benzoyl-6-vinyl-5,6-dihydro-2*H*-pyran-2-one (**5a**): Colorless gum. IR: 1775, 1750, 1690, 1600, 1580. UV: 254 (10900). ^{1}H-NMR: 2.13 (3H, s, COC$\underline{H}_3$), 2.81 (1H, dd, J=3, 18 Hz, H-5), 3.53 (1H, dd, J=6, 18 Hz, H-5), 5.44 (1H, d, J=11 Hz, CH=C$\underline{H}_2$), 5.60 (1H, d, J=17 Hz, CH=C$\underline{H}_2$), 6.19 (1H, dd, J=11, 17 Hz, C$\underline{H}$=CH$_2$), 6.43 (1H, dd, J=3, 6 Hz, H-4), 7.4—7.6 (3H, m, ArH), 8.0—8.1 (2H, m, ArH). ^{13}C-NMR: 20.1 (q, CO$\underline{C}$H$_3$), 31.7 (t, C-5), 89.9 (s, C-6), 118.3 (t, CH=C$\underline{H}_2$), 128.3 (d×2, Ph), 129.0 (d, C-4), 130.4 (d×2, Ph), 133.5 (d, C$\underline{H}$=CH$_2$), 133.8 (s, Ph), 135.4 (d, Ph), 137.8 (s, C-3), 157.9 (s, C-2 or C$\underline{O}$CH$_3$), 168.1 (s, C$\underline{O}$CH$_3$ or C-2), 196.5 (s, PhC$\underline{O}$). CI-MS m/z: 287 (MH^+), 57 (base peak).

3-Acetoxy-6-benzoyl-6-phenyl-5,6-dihydro-2*H*-pyran-2-one (**5b**): Colorless needles from Et_2O–$CHCl_3$, mp 141—142 °C. IR: 1765, 1740, 1675, 1600, 1580. UV: 252 (12100). ^{1}H-NMR: 2.16 (3H, s, COC$\underline{H}_3$), 2.90 (1H, dd, J=3, 18 Hz, H-5), 3.76 (1H, dd, J=6, 18 Hz, H-5), 6.50 (1H, dd, J=3, 6 Hz, H-4), 7.3—7.7 (8H, m, ArH), 7.8—7.9 (2H, m, ArH). CI-MS m/z: 337 (MH^+), 295 (base peak). *Anal.* Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.25; H, 4.96.

X-Ray Crystallographic Analysis of 3e The reflection data were collected on a Rigaku AFC-5 four-circle diffractometer controlled by the MSC/AFC program package, using graphite-monochromated Mo K_α radiation with the ω-2θ scan technique to a maximum 2θ of 55° at a scan speed of 6°/min. A total of 5312 reflections was collected. The structure was solved by the direct method[8] using the TEXSAN crystallographic software package. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically or placed at the calculated positions. The final cycle of full-matrix least-squares refinement was performed using 1903 reflections with $I>3.0\delta$ (I).

Crystal data of **3e**, colorless prisms from benzene, 195—197 °C: $C_{21}H_{21}NO_6Si$. M_r=411.49, orthorhombic, a=14.641(2), b=21.794(5), c=13.067(2) Å, b=93.57(1)°, V=4169(1) Å^3, D_c=1.39 g/cm^3, Z=8. Space group, P_{bca}; crystal size, 0.4×0.2×0.5 mm. R=0.043.

The coordinates of all hydrogen atoms, bond distances, and bond angles for this structure have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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