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# PHOTOCHEMISTRY OF *o*-METHYL-SUBSTITUTED AROMATIC KETONE WITH 5-ISOBUTYLIDENE-1,3-DIOXANE-4,6-DIONE DERIVATIVES

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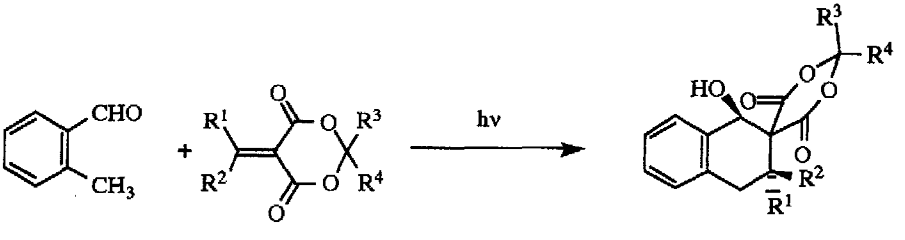
*Key Words:* Photochemistry; *o*-Methyl-substituted Aromatic Ketone; Photoenol; 5-Isobutylidene-1,3-dioxane-4,6-dione; Addition Reaction

**Abstract:** *Photolyses of o-methylacetophenone or o-methylbenzophenone with 5-isobutylidene-1,3-dioxane-4,6-diones produced novel adducts, bonding between the β-carbon of the acylales and the o-methyl carbon of the aromatic ketones.*

The intramolecular hydrogen abstraction of *o*-alkyl-substituted aromatic carbonyl compounds by UV irradiation has been extensively investigated.[1,2] The transient (*E*)-photoenols undergo Diels-Alder reaction with some dienophiles.[1b,1c,3] In a preceding paper,[3] we reported that the photoenol of *o*-methylbenzaldehyde (**1**) reacted with 5-alkylidene-1,3-dioxane-4,6-dione derivatives **2**, effective unsymmetrical dienophiles, leading stereo- and regioselectively to the spiro- and polyspirocyclic compounds **3**, with 1,2,3,4-tetrahydro-1-naphthol structures (Scheme 1).

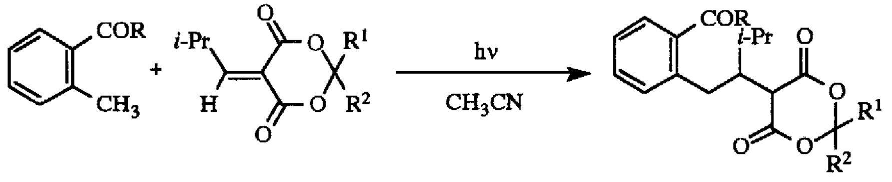


**1** **2** **3**

Scheme 1

We wish to communicate here the results obtained by photolyses of *o*-methylacetophenone (**4**) and *o*-methylbenzophenone (**5**) with 5-isobutylidene-1,3-dioxane-4,6-dione derivatives **2a-c**.
An equimolar solution (0.02 mol dm$^{-3}$) of **4** and **2a-c** in acetonitrile (400 cm$^{3}$) was irradiated at room temperature under an argon atmosphere using a 100-W high-pressure mercury lamp with a Pyrex jacket. The reaction was monitored by the disappearance of **4** or **2a-c** on TLC. After evaporation of the solvent, the photoproducts were isolated by silica gel column chromatography using acetone-hexane (5:95, *v/v*) as the eluent. The major photoproducts **6**, **7**, and **8**, were obtained in 47%, 62%, and 67% yields, respectively, which are bonding between the β-carbon of **2a-c** and the methyl carbon of **4** (Scheme 2), and were not the expected

[4π+2π]cycloadducts. In addition, 1-hydroxy-1-methyl-4*H*-2,3-benzodioxine,[4] a peroxide formed by the cycloaddition of the photoenol of **4** with oxygen, was obtained as a minor photoproduct (~5%). The peroxide was not formed when a completely degassed solution was irradiated.



**4**: R=CH$_3$
**5**: R=Ph

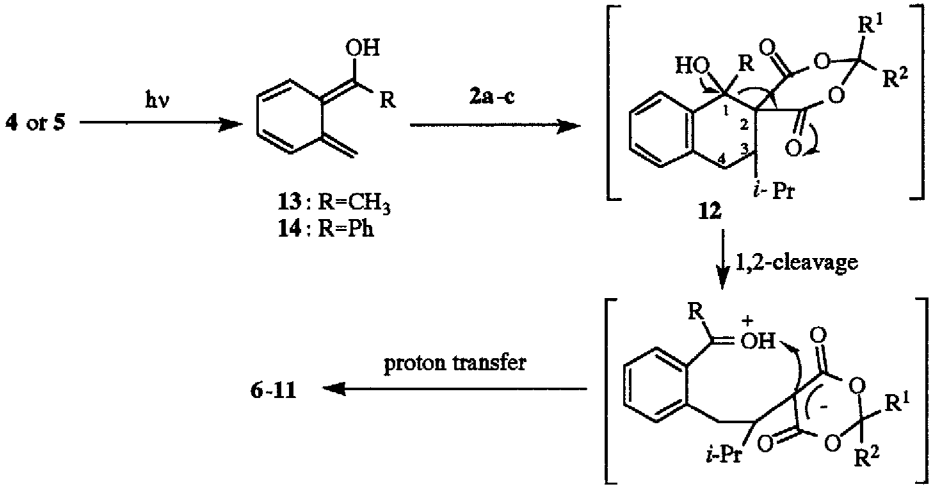
**2a**: R$^1$=R$^2$=CH$_3$
**2b**: R$^1$-R$^2$=-(CH$_2$)$_4$-
**2c**: R$^1$-R$^2$=-(CH$_2$)$_5$-

**6**: R=R$^1$=R$^2$=CH$_3$
**7**: R=CH$_3$, R$^1$-R$^2$=-(CH$_2$)$_4$-
**8**: R=CH$_3$, R$^1$-R$^2$=-(CH$_2$)$_5$-
**9**: R=Ph, R$^1$=R$^2$=CH$_3$
**10**: R=Ph, R$^1$-R$^2$=-(CH$_2$)$_4$-
**11**: R=Ph, R$^1$-R$^2$=-(CH$_2$)$_5$-

Scheme 2

Similarly, the photolyses of *o*-methylbenzophenone (**5**) with **2a-c** gave the corresponding adducts **9**, **10**, and **11**, were produced in 36%, 21%, and 24% yields, respectively, although an appreciable amount of polymeric material was formed. Furthermore, 5-isobutyl-1,3-dioxane-4,6-diones,[5] the reduction compounds of **2a-c** were obtained as by-products in 10~12% yields.

The structure of these adducts was elucidated by means of NMR and other spectroscopic measurements.[6] The NMR and IR spectra of the adducts **6-11**, show the presence of acetyl or benzoyl group with no hydroxyl group. In the $^1$H NMR spectra, the α-methine protons of **6-11** act as Brønsted acid which appeared as a doublet with $J$=1.4-2.3 Hz at δ 3.5-3.7 ppm in CDCl$_3$, and during the measurement after adding CD$_3$OD, an incorporation of deuterium into the α-methine group was detected. On the other hand, each ortho methylenic proton of **6-11** was observed at different magnetic fields and the coupling constants between the ortho methylenic protons have a $J$=12.7-13.8 Hz.



Scheme 3

Since it is generally recognized that the smaller the energy gap between the HOMO of the diene and the LUMO of the dienophile, the more easily the Diels-Alder reaction proceeds,[7] we performed a MO calculations[8] for **2a** and photoenols **13** and **14**, of **3** and **4**. For the purpose of the comparison with the energy levels of **13** and **14**, the photoenol of *o*-methylbenzaldehyde (**1**), (*E*)-α-hydroxy-*o*-quinodimethane (**15**), was also calculated. The HOMO levels of **13**, **14**, and **15** were obtained as -8.046, -7.981, and -7.812 eV, respectively, while the LUMO level of **2a** was calculated as -1.034 eV. Consequently, the energy gaps between **13**-**15** and **2a** are similar. Since the Diels-Alder reaction of the enol **15**, with **2a** proceeded[3] and the life-times of **13** and **14** in cyclohexane have 4.3 s[2h] and 10 s,[2j] respectively, the reaction pathway is considered as follows. The [4π+2π]cycloadducts **12**, produced by the Diels-Alder reaction of the enols **13** and **14**, undergo the 1,2-cleavage with proton transfer due to the steric hindrance between the spirocyclic acylale at the 2-position and the phenyl or methyl and hydroxyl groups at the 1-position on the 1,2,3,4-tetrahydro-1-naphthol system to afford the adducts **6**-**11** (Scheme 3).

It has been reported that the heterocycloadducts, which were derived by the cycloaddition of the photoenol of the *o*-alkyl-substituted aromatic carbonyl compounds with oxygen[4,9] or sulfur dioxide,[10] undergo cleavage between the hetero atoms or between the hetero atom and carbon atom. However, there is no known example of the 1,2-cleavage in the 1,2,3,4-tetrahydro-1-naphthol ring produced by the Diels-Alder reaction with dienophiles.

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**9**: colorless crystals; mp 110-111°C (from benzene-hexane); IR (KBr) 3063, 3000, 2963, 2858, 1782, 1748, 1663 cm$^{-1}$; $^1$H NMR (90 MHz, $CDCl_3$) δ 0.81(3H, d, *J*=6.6 Hz), 1.04(3H, d, *J*=6.6 Hz), 1.7-2.2(1H, m, $C\underline{H}(CH_3)_2$), 1.72(3H, s), 1.76(3H, s), 2.2-2.8(1H, m), 2.91(1H, dd, *J*=11.9 and 13.8 Hz), 3.10(1H, dd, *J*=5.8 and 13.8 Hz), 3.70(1H, d, *J*=1.7 Hz, α-CH), 7.2-7.9(9H, m, aroma-H); $^{13}$C NMR (22.5 MHz, $CDCl_3$) δ 21.04(q), 21.42(q), 26.70(q), 28.18(q), 29.5(d), 34.22(t), 45.50(d, α-C), 48.13(d, β-C), 104.76(s), 126.18(d), 128.31(d), 128.46(2C, d), 130.36(2C, d), 130.43(d), 131.16(d), 133.55(d), 137.31(s), 139.06(s), 139.74(s), 164.92 (s), 166.90(s), 198.84(s, PhCO).

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