Photochemistry of 1-Aryl-1,2-propanediones. Intermediacy of an Enol in the Photocyclization of 1-(*o*-Tolyl)-1,2-propanedione[1]

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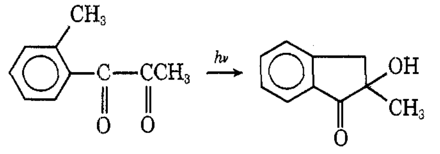
An enol (4), a precursor for photocyclization of 1-(*o*-tolyl)-1,2-propanedione (1) to 2-hydroxy-2-methylindanone (2), was trapped in the photolysis of 1 in the presence of an equivalent amount of dimethyl acetylenedicarboxylate as its cyclic adduct (3). The obtained adduct 3 was thermally unstable and decomposed at 180° to a mixture of the product (2), the starting diketone (1), and dimethyl acetylenedicarboxylate. This fact suggests that the photocyclization of 1 to 2 may proceed *via* an enol (4) formed by 1,5-hydrogen migration, but not the apparent 1,6 shift. Further, this is in accordance with the fact that a methylene analog to 1, α-(o-tolyl)acetone, gives the corresponding reduction product, but not the corresponding indene.

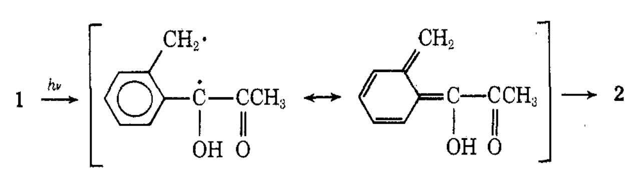
Photocyclization of 1-(*o*-tolyl)-1,2-propanedione (1) to 2-hydroxy-2-methylindanone (2) was reported by Bishop and Hamer.[2] It is ambiguous in the photocyclization which of the carbonyl oxygens initially abstracts a methyl hydrogen atom.



1 2

While 1,6-hydrogen migration from ortho methyl to the excited acetyl carbonyl oxygen can lead directly to the product (2), 1,6-hydrogen migration in general is not common in cases where the 1,5-hydrogen shift can operate.[3] The 1,6 shift seems to be limited to carbonyl systems which have no γ-hydrogen or have a δ-hydrogen atom activated by alkoxy or other groups.[4,5] A more common 1,5 shift to give enol (*e.g.*, the enol 4) followed by a 1,2 shift produces the overall effect of a 1,6 shift. However, Bishop and Hamer have discarded the intervention of enol 4 at any stage of the reaction since no deuterium incorporation into the product (2) occurs in photolysis in methanol-*O*-*d*.[1a]

We have reexamined the question of the intermediacy of the enol 4 in the photocyclization and wish to present some evidence for an initial 1,5-hydrogen transfer to aroyl carbonyl oxygen leading to the enol.



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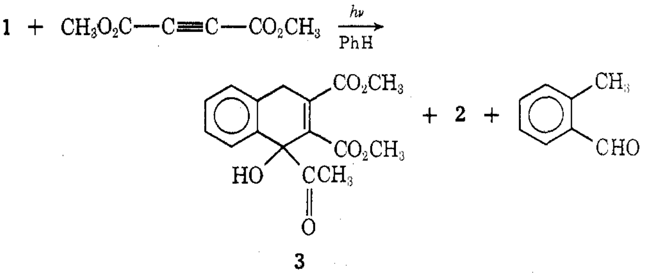
A solution of 1 (3.5 mmol) and dimethyl acetylenedicarboxylate (3.6 mmol) in benzene (120 ml) was irradiated for 6 hr under a nitrogen atmosphere. The reaction mixture was condensed *in vacuo* and the products were separated by silica gel chromatography, yielding unreacted starting diketone (trace), dimethyl acetylenedicarboxylate (trace), 2-tolualdehyde (14.5%), an adduct (3, 5.7%), and 2 (51.7%). An adduct (3) was isolated as a viscous, pale yellow oil which could not be crystallized. The infrared absorption of this material clearly showed the presence of hydroxyl (3400 cm^{-1}) and two sorts of carbonyl (1710 and 1680 cm^{-1}), but the absence of the acetylenic triple bond (2200 cm^{-1}). In addition, its nmr spectrum showed two carbomethoxy methyl (6 H, τ 6.23), an acetyl methyl (3 H, τ 7.78), and a broad hydroxylic proton (1 H, τ 1.20) which is exchangeable with D_2O. The mass spectrum of the material (M^+ 304) as well as the nmr peaks and the integration of the nmr bands (see Experimental Section) was consistent with the molecular formula $C_{16}H_{16}O_6$ and structure 3.



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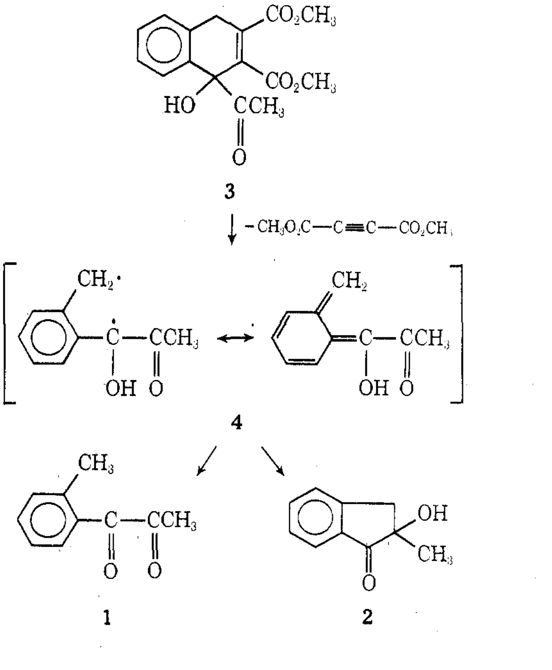
Interestingly, compound 3 is thermally unstable. Thus, the adduct 3 decomposed on passing through a glc column at 180° to yield the two starting materials 1 and dimethyl acetylenedicarboxylate and the cyclization product 2 (molar ratio of two products 1:2 was 2:3). Adduct 3 itself could not be detected by the glc method on account of the thermal instability.

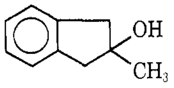
$$3 \xrightarrow{180°} 1 + 2 + CH_3O_2C{-}C{\equiv}C{-}CO_2CH_3$$

The observation is important because it demonstrates that an enol (or its resonance structure, diradical 4) expected from the pyrolysis of 3 can either cyclize or return to 1.



The above thermal reaction of **3** to **2** correlates with the photochemical process of **1** to **2**, since it shows the possibility of 1,6-cyclization of a 1,4-diradical or enol (**4**) which may be formed by 1,5-hydrogen transfer from ortho methyl to aroyl carbonyl oxygen. However, this cannot preclude the possibility of a competitive pathway, a direct 1,6-hydrogen shift (*via* a seven-membered transition state).

Finally, an attempt to photocyclize a monoketone analog, α-(*o*-tolyl)acetone (**5**), to the corresponding indene (**6**) for the examination of the possibility of 1,6-hydrogen abstraction was made. Irradiation of a 2-propanol solution (0.09 *M*) of α-(*o*-tolyl)acetone (**5**) yielded mainly 1,2-di(*o*-tolyl)ethane (**7**, 29.3%) and a pinacol (**8**, 14%), but the corresponding indene was absent. Failure to observe cyclization to **6** in spite of the proximity of ortho methyl and acetyl oxygen suggests that there is little tendency for a 1,6 shift.



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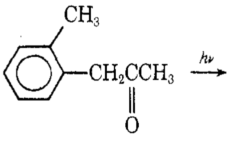

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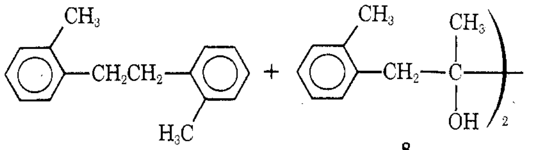

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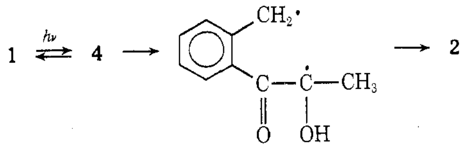
In summary, a 1,4 diradical or its resonance form **4** may be converted to a 1,5 diradical (**9**) by 1,2-hydrogen shift and then cyclization to **2**. Indeed, such 1,2-hydrogen shift was reported for α-diketone radical[6] (**9**).



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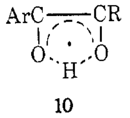
The pathway *via* 1,5 shift seems to be inconsistent with the fact that no deuterium incorporation into **2** is observed in methanol-*O*-*d*. However, an assumption of the stabilization of **4** *via* hydrogen bonding (**10**) can account for this phenomenon.



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Experimental Section

Infrared spectra were determined with a Perkin-Elmer grating infrared spectrophotometer, Model 337. The nmr spectra were determined with a Japan Electron Optic Laboratory Co. C60 HL nmr instrument. Mass spectra were determined with a Hitachi RMS-4 mass spectrometer. Gas chromatograms were recorded with a Yanaco GCG-550F gas chromatograph with a flame ionization detector (a 2 m × 2.5 mm column packed with 5% SE-30 on Chromosorb at 100–250°). The irradiation was carried out using a Halos 300-W high-pressure Hg lamp which emits over 300-nm light through a Pyrex filter.

Materials. 1-(*o*-Tolyl)-1,2-propanedione (**1**) was prepared by a method similar to Hartung's procedure,[7] bp 128–137° (20 mm). α-(2-Toyl)acetone (**5**) was prepared by the reaction of α-(*o*-tolyl)-acetyl chloride with methylzinc iodide in ethyl acetate as a pale yellow oil: bp 110–113° (14–15 mm) [lit.[8] bp 122° (23 mm)]; nmr (CCl_4) τ 2.94 (s, 4 H, phenyl), 6.32 (s, 2 H, methylene), 7.80 (s, 3 H, $COCH_3$), and 8.02 (s, 3 H, tolyl methyl).

Reaction of 1 with Dimethyl Acetylenedicarboxylate. A benzene solution (120 ml) of an equimolar mixture of **1** (567 mg) and dimethyl acetylenedicarboxylate (513 mg) was irradiated for 6 hr until the yellow color of the solution had disappeared. The concentrated reaction mixture was chromatographed on a 15 × 300 mm column, slurry packed in benzene–5% acetone as an eluent. Fractions 5–10 (each 5 g) were a mixture of dimethyl acetylenedicarboxylate and the starting diketone (trace). Fractions 38–40 were 2-tolualdehyde (61 mg). Fractions 41–44 yielded a viscous, pale yellow oil, an adduct (**3**, 61 mg). Thin layer chromatography on Kiesel Gel G (Merck) with benzene–5% acetone showed one spot at R_f 0.24. The adduct **3** had the following spectra: ir ν_{max} (liquid film) 3400, 3050, 2940, 1710, 1680, 1425, 1340, 1275, 1150, and 740 cm^{-1}; nmr (CCl_4) τ 1.20 (s, 1 H), 2–3 (m, 4 H), 5.98 (s, 2 H), 6.23 (s, 6 H), and 7.78 (s, 3 H); mass spectrum *m/e* (rel intensity) 28 (100), 39 (25), 43 (50), 44 (25), 45 (20), 65 (20), 77 (20), 91 (64), 105 (20), 115 (20), 118 (60), 119 (66), 129 (15), 133 (20), 136 (50), 145 (63), 160 (25), 161 (22), 213 (10), 221 (25), 245 (17), 262 (5), and 304 (10). The adduct (**3**) was completely decomposed in a glc column (SE-30 on Chromosorb) at 180° as the injection temperature to yield **1** and **2** (**2**:**1** = 1.5 based on their relative peak area) as well as dimethyl acetylenedicarboxylate (column temperature 100–250°). Fractions 55–70 were 2-hydroxy-2-methylindanone (**2**, 293 mg), mp 53–54.5°. The indanone **2** had the following spectra: ν_{max} (KBr) 3400, 2960, 2910, 1715, 1145, and 730 cm^{-1}; λ_{max} (MeOH) 245 and 290 nm; nmr (CCl_4) τ 2.5 (m, 4 H), 6.0 (s, 1 H), 6.84 (s, 2 H), 8.63 (s, 3 H); mass spectrum *m/e* (rel intensity) 43 (100), 50 (40), 64 (15), 65 (15), 76 (13), 91 (42), 105 (13), 120 (30), 146 (13), and 162 (25).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.5; H, 6.22.

Photolysis of α-(*o*-Tolyl)acetone (5). A 2-propanol solution (30 ml) of the ketone (507 mg) was irradiated for 10 hr in a quartz vessel without a Pyrex filter under N_2 atmosphere, giving three isolated products. The first eluted product was di(2-tolyl)ethane (**7**, 29.3%): mp 66°; nmr (CCl_4) τ 2.94 (s, 8 H), 7.20 (s, 4 H), and 7.74 (s, 6 H). Although the second product was unidentified yet, it was not a hydroxylic compound (*e.g.*, indene **6**), because its nmr spectrum shows the absence of an acetyl group and a hydroxyl group which was confirmed by no signal change by addition of D_2O in a range of τ −10 to 10. The third eluted product was a pale yellow liquid (a pinacol, **8**, 14%): nmr (CCl_4) τ 2.93 (s, 8 H), 5.60 (s, 2 H, OH exchangeable with D_2O), 7.10 (s, 4 H), 7.70 (s, 6 H), and 8.82 (s, 6 H); ν_{max} (liquid film) 3400, 1700, 1150, and 740 cm^{-1}; mol wt (mass spectrum) 298 (M^+) (calcd for $C_{20}H_{26}O_2$, 298).

Registry No.—**1**, 25412-56-0; **2**, 25412-59-3; **3**, 51051-99-1; **5**, 51052-00-7; **7**, 952-80-7; dimethyl acetylenedicarboxylate, 762-42-5.

References and Notes

(1) Contribution No. 193.

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