

PHOTOCHEMICAL SYNTHESIS OF 1,4-DIKETONES VIA THE  
1,3-ACYL SHIFT OF  $\alpha$ -HYDROXY- $\beta,\gamma$ -UNSATURATED KETONES

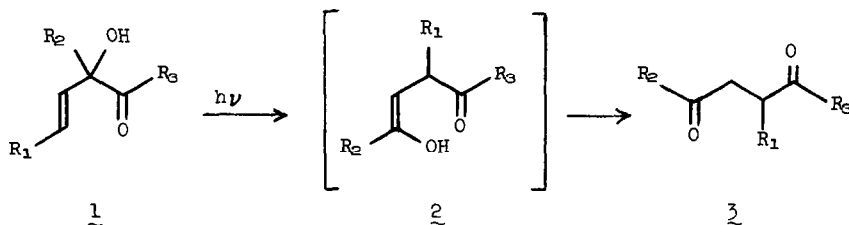
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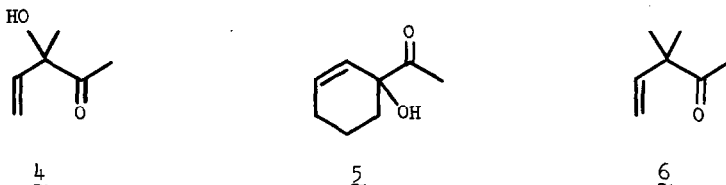
Our interest in the complex photochemistry of  $\beta,\gamma$ -unsaturated ketones<sup>1</sup> and other 1,4-bichromophoric molecules<sup>2</sup> has generated efforts to harness their diverse photochemical reactions to synthetic designs. Properly designed molecular segments could, for example, be used as latent functional groups, capable of rearranging to the desired functionality under the mild conditions of photolysis. Thus,  $\alpha$ -hydroxy- $\beta,\gamma$ -unsaturated ketones (1) might be attractive as masked 1,4-diketones (3), to which they could be converted via photochemical 1,3-acyl shifts and subsequent tautomerization of a transient  $\gamma$ -keto enol (2); i.e., 1  $\xrightarrow{h\nu}$  [2]  $\rightarrow$  3. Communication of our results, which demonstrate (a) the workability of the 1,4-di-



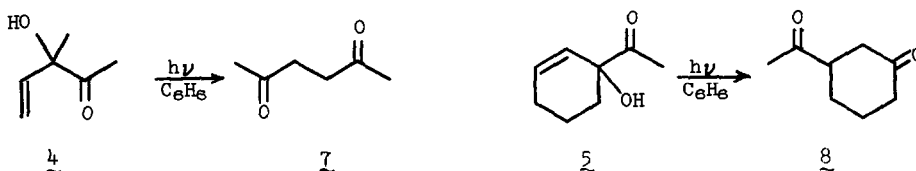
ketone synthesis, and (b) typical  $\beta,\gamma$ -unsaturated ketone mechanistic surprises, to which the  $\alpha$ -hydroxy substituent apparently contributes, is prompted by the related findings of Sasaki,<sup>3</sup> Carlson,<sup>4</sup> and McMurry,<sup>5</sup> et al. However, the  $\beta,\gamma$ -unsaturated ketones studied by Sasaki, et al.<sup>3</sup> and McMurry, et al.<sup>5</sup> were also  $\alpha,\beta$ -unsaturated; hence, their suitability as mechanistic models for systems in which the  $\beta,\gamma$ -unsaturated ketone is an isolated chromophore is uncertain.

3-Hydroxy-3-methylpent-4-en-2-one (4) and 1-acetylcyclohex-2-en-1-ol (5) were selected as systems in which molecular conformational effects other than hydrogen bonding<sup>3</sup> should provide no special assistance to the 1,3-acyl shift. For example, the 1,3-shift product from

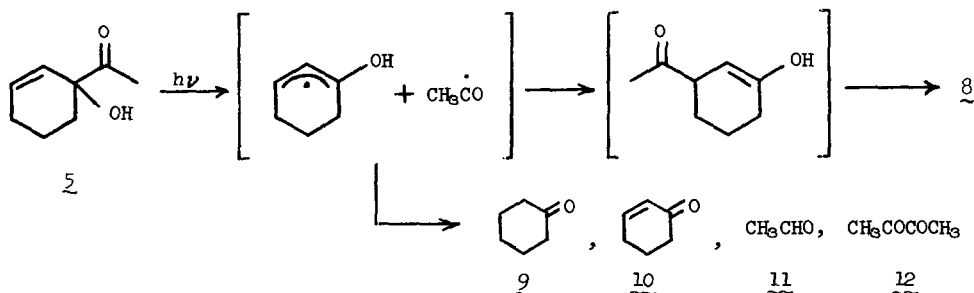
3,3-dimethylpent-4-en-2-one (6), a close analog of 4, accounts for but 22% of reacted 6,<sup>8</sup> whereas 1,3-shift products are often predominant in cyclic systems.<sup>1</sup> Unsaturated ketols 4 and 5 were synthesized from methyl vinyl ketone and cyclohex-2-en-1-one, respectively, by addition of 2-lithio-2-methyl-1,3-dithiane and subsequent hydrolysis of the dithiane-carbonyl adducts with mercuric chloride in calcium carbonate-buffered 80% aqueous acetonitrile.<sup>7</sup>



Irradiation of ca. 1 M degassed solutions of 4 ( $\lambda_{\max}$  [c-C<sub>6</sub>H<sub>12</sub>] 280 nm,  $\epsilon$  148) in benzene (alternatively, dioxane) containing hexadecane as internal standard with a Pyrex-filtered mercury arc to 98% destruction of 4 produced a mixture from which 2,5-hexanedione (7) was isolated as the predominant photoproduct (87% of volatiles);<sup>8</sup> 7 was identified by comparison of spectra with those of authentic material.



Similarly, irradiation of 5 ( $\lambda_{\max}$  [c-C<sub>6</sub>H<sub>12</sub>] 282 nm,  $\epsilon$  67) in degassed benzene to 86% reaction gave 3-acetylcyclohexanone (8), identified by comparison of spectra with material synthesized by the methods of McCoubrey<sup>9</sup> and Corey and Crouse,<sup>7a</sup> as the major product (78%<sup>8</sup> of volatile products). Cyclohexanone (9) was the most abundant by-product (13%); however, traces of cyclohex-2-en-1-one (10), acetaldehyde (11), biacetyl (12), and five unidentified

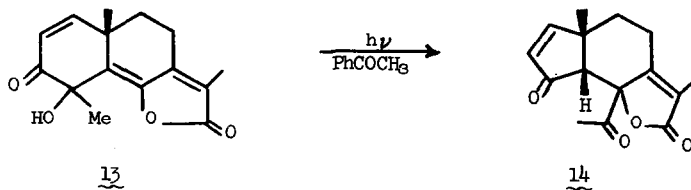


substances were detected by glpc. The major products 7 and 8 are those expected from formal 1,3-acetyl shifts occurring through  $\alpha$ -cleavage, recombination of intermediate acetyl-allylic radical pairs, and tautomerization. Unlike most 1,3-shifts, however,<sup>1</sup> the 4  $\rightarrow$  7 and 5  $\rightarrow$  8 transformations are rendered irreversible by the final tautomerization. The by-products 9 - 12 support the stepwise formulation for the 1,3-shift involving discrete acetyl and allylic radical intermediates, but do not exclude the possibility of a concerted shift occurring as a mechanism parallel to and competing with the  $\alpha$ -cleavage which leads to the by-products.

Consistent with the norm established for  $\beta,\gamma$ -unsaturated ketones, wherein  $\alpha$ -cleavage and 1,3-acyl shifts originate from singlet excited states, the 4  $\rightarrow$  7 rearrangement could not be sensitized with xanthone,<sup>10</sup> nor appreciably quenched with 1,3-cyclohexadiene. Failure to sensitize an  $\alpha$ -hydroxy- $\beta,\gamma$ -unsaturated ketone's 1,3-shift was also noted by Sasaki<sup>9</sup> and Carlson.<sup>4</sup>

However, the conversion of 5 to 8 was photosensitized with 0.15 M xanthone and 350-nm lamps. Although control runs indicated stray light effected some direct reaction as well, the sensitized irradiations of 5 at 350 nm were ca. three times more efficient. Furthermore, conversion of 5 to 8 was partially quenched by addition of 2 M 1,3-cyclohexadiene. Although such high quencher concentrations admit the possibility of singlet quenching, glpc analysis (5-ft x 0.25-in. 20% Carbowax 20M on 60/80 firebrick, 150°) of quenched photolysates revealed formation of those cyclohexadiene photodimers we observed as photoproducts of the 1,3-cyclohexadiene triplet<sup>12</sup> rather than the singlet.<sup>13</sup> Thus, it seems probable that the photochemistry of 5 involves a rare<sup>6</sup> triplet-state 1,3-acyl shift. Whether or not there is also a singlet-state component to the direct irradiation 1,3-shift is not yet clear. Quantum yield studies are needed to measure the partitioning between singlet and triplet reactions. Clearly, however, the 5  $\rightarrow$  8 triplet-state reaction is an anomaly; all other 1,3-acyl shifts in  $\alpha$ -hydroxy- $\beta,\gamma$ -unsaturated ketones<sup>3,4</sup> are singlet reactions.

The only prior report of triplet-state reactivity in an  $\alpha$ -hydroxy- $\beta,\gamma$ -unsaturated ketone was the acetophenone-sensitized conversion of the 4-hydroxysantonenes (13) to the 1,4-diketone 14.<sup>5</sup> Unlike the present case, however, the 13  $\rightarrow$  14 reorganization apparently involves the



1,2-acyl shift common for triplet states and subsequent ring opening of the hydroxycyclopropyl ketone which would presumably be the initial oxa-di-pi-methane reaction product. However, since only trace photoproducts of 5 remain unidentified, mechanisms similar to that involved in the 13 → 14 transformation cannot be major reaction pathways in the photochemistry of 5. No satisfying explanation for the atypical behavior of 5 is readily apparent.

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#### References and Notes

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8. Although 7 and 8 are by far the major volatile components of photolysates of 4 and 5, respectively, polymerization reduces the overall yields to 35% of 7 and 22% of 8.
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10. The non-reactivity of triplet 4 and of triplet 2-hydroxy-2-(2-methyl-1-propenyl)cyclohexanone<sup>4</sup> may be another manifestation of the free-rotor effect.<sup>1,11</sup>
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