

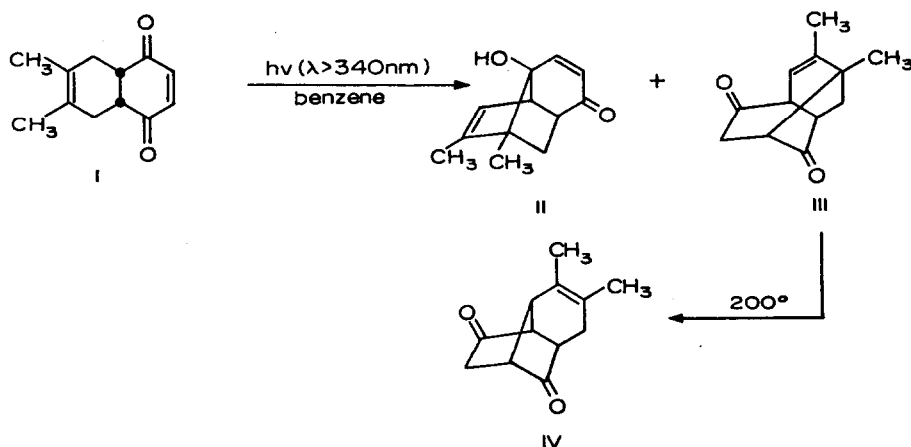
SOLUTION PHOTOCHEMISTRY. IX¹
A NOVEL DOUBLE REARRANGEMENT OF A β,γ -UNSATURATED KETONE.

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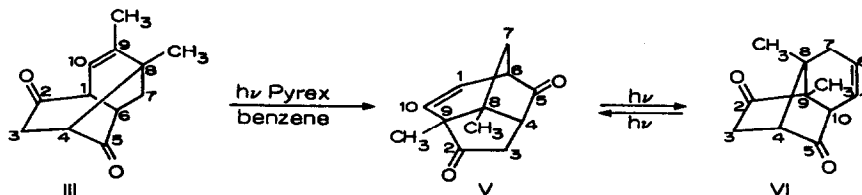
Recent work in our laboratory has shown that $n \rightarrow \pi^*$ excitation of the *p*-benzoquinone-2,3-dimethylbutadiene Diels-Alder adduct I in benzene with light of wavelength greater than 340 nm leads to the rearranged products II and III (1,3).



Photoproduct III was found (1) to be quantitatively converted to IV upon sealed tube thermolysis at 200° (4) but was stable to light of $\lambda > 340\text{ nm}$ since it has very little absorption in that region. We would like to report in the present communication that irradiation of III in its $n \rightarrow \pi^*$ absorption band (uv max (MeOH) 292 nm, ϵ 220) leads to two novel photoproducts, the major one of which (VI) possesses the basic ring system of IV but with relocation of the methyl groups and the double bond.

Thus irradiation (100 W Hanovia) of a 5×10^{-3} M benzene solution of III through Pyrex slowly gave rise to a single new photoproduct subsequently shown to have structure V. After 8 hours, starting material III had disappeared, and further irradiation gradually led

to a second new compound VI at the expense of V until, after 48 hours, the V:VI ratio was time-invariant at 1:1.9. No other products were detectable by vapor phase chromatography (5).



Photoproducts V and VI were easily separable by preparative vapor phase chromatography and could be isolated in this way in a combined yield of 50%. That the final V:VI = 1:1.9 ratio is the result of a true photochemical equilibrium was shown by irradiation of pure samples of both V and VI; each gave rise to the same V:VI = 1:1.9 mixture within experimental error; no III could be detected in either of these photolyses.

The isomeric relationship of compounds III, V, and VI was proved by mass spectrometry and elemental analysis. The structures of photoproducts V and VI were assigned on the basis of mechanistic reasoning (see later) and on the following spectroscopic data: Photoisomer V, mp (sealed tube) 166-168°, showed an $n \rightarrow \pi^*$ uv max (MeOH) of 292 nm (ϵ 460), sh 285 nm (ϵ 400), and sh 307 nm (ϵ 410). Photoproduct VI, mp (sealed tube) 184-187° dec, exhibited an $n \rightarrow \pi^*$ uv max (MeOH) of 290 nm (ϵ 110). These uv spectra possess the fine structure, λ_{\max} positions, and enhanced extinction coefficients characteristic of β,γ -unsaturated ketones (6). As is reasonable, product V, which is doubly β,γ -unsaturated, has the more intense absorption. Also indicative were the infrared carbonyl stretching frequencies of V and VI; both exhibited intense absorptions characteristic of strained five-membered ring ketones, 5.73 μ for V and 5.70 μ for VI. Hydrogenation of V and VI provided the corresponding dihydro derivatives (no vinyl hydrogens in the nmr), mp (sealed tube) 225° dec and 211-212.5° respectively. The ir carbonyl stretching frequencies of dihydro V and VI were unchanged relative to V and VI themselves indicating the absence of an α,β -unsaturated carbonyl chromophore in either V or VI. As expected, hydrogenation removed the characteristic β,γ -unsaturated ketone uv absorptions associated with V and VI.

The nmr spectrum (CCl_4) of V was most informative. The C_{10} vinyl hydrogen appeared

as a clean doublet at τ 4.78 with $J_{1,10} = 9$ Hz. The C_1 vinyl hydrogen (τ 4.07) was a multiplet which collapsed to a doublet, $J_{1,10} = 9$ Hz, upon irradiation of the multiplet due to the C_6 methine at τ 7.00. Additional signals appeared at τ 7.71 (m, 3, C_3 methylene and C_4 methine), 8.27 (m, 2, C_7 methylene), 8.88 (s, 3, Me), and 8.95 (s, 3, Me). The nmr spectrum (CCl_4) of VI, while supportive, was less clear-cut. It consisted of signals at τ 4.17 (m, 2, vinyls), 7.38-7.90 (m, 6), 9.04 (s, 3, Me), and 9.07 (s, 3, Me).

The photochemically initiated $III \rightarrow V$ and $V \rightleftharpoons VI$ conversions have ample literature precedent and are examples of a process which appears to be general for β,γ -unsaturated ketones in their excited singlet states, namely, 1,3-acyl migration (7). Thus V is derived from III via a C_1 to C_9 shift of the C_2 acyl carbon, and VI similarly arises from V through a C_6 to C_{10} migration of the C_5 acyl group. Singlet excited states are implicated in these reactions as well since piperylene failed to significantly affect their rates or product ratios, and the use of common triplet-energy sensitizers led either to no reaction or to polymer formation. The predominance of VI in the photochemical $V \rightleftharpoons VI$ is likely due in part to its reduced extinction coefficient at the wavelengths employed, although common excited state partitioning factors must also play a role since the proportionality is not direct.

Finally, the most significant aspect of this work may lie in the fact that it provides a second (4) facile photochemical entry (via VI) into the basic ring system found in several sesquiterpenes (e.g., copacamphor, copaborneol, copaisoborneol, copacamphene, and sativene) and allows for the specific introduction of substituents at positions which were previously inaccessible.

ACKNOWLEDGEMENT

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2. National Research Council Predoctoral Fellow, 1968 - present.
3. For related work on this rearrangement see J.R. Scheffer, J. Trotter, R.A. Wostradowski, C.S. Gibbons, and K.S. Bhandari, J. Amer. Chem. Soc., 93, 3813 (1971).
4. Photoproduct IV is also formed in 80% isolated yield from the photolysis of I in tert-butyl alcohol with light of wavelength greater than 340 nm (1).
5. Analytical vpc was carried out using a 5' x 1/4" stainless steel column packed with 10% FFAP on 60/80 Chromosorb W at a column temperature of 150° and a helium flow rate of 150 ml/min. Preparative vpc was done on a 10' x 1/4" stainless steel column packed with 30% DEGS on 60/80 Chromosorb W at 170° and 120 ml/min.
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