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WAVELENGTH DEPENDENT PHOTOISOMERIZATION OF BICYCLO[3.1.0]HEXENONES

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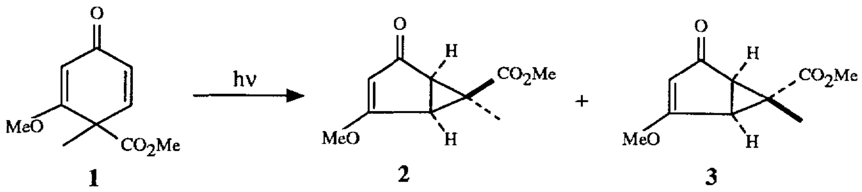
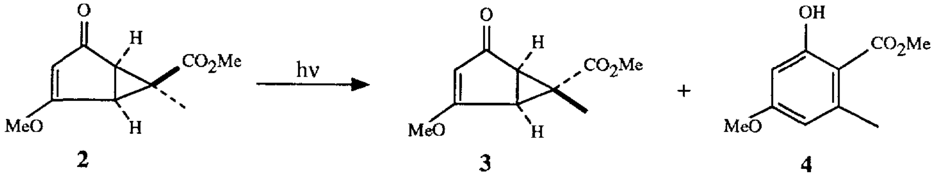
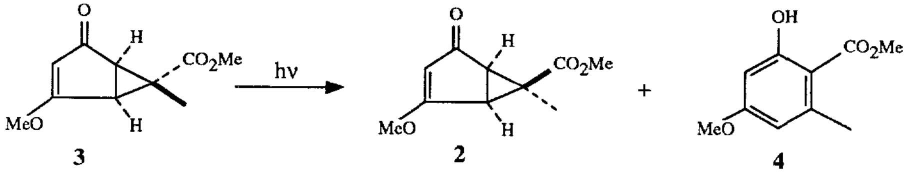
Abstract: The unusual wavelength dependent product selectivity observed upon irradiation of a substituted 2,5-cyclohexadien-1-one is shown to result from wavelength dependent quantum yields for rearrangement of the primary photoproduct bicyclo[3.1.0]hexenones. Reaction selectivity can be optimized by careful choice of irradiation wavelength and length of irradiation time.

Many mechanistic studies of the 2,5-cyclohexadien-1-one to bicyclo[3.1.0]hexenone photorearrangement and the related rearrangements of bicyclo[3.1.0]hexenones have been reported,[2] including a recent study which was aimed at the development of the rearrangements for organic synthesis.[3] Several factors are of interest from a synthetic viewpoint, including the ready availability of a range of 4-alkyl-4-(methoxycarbonyl)-2,5-cyclohexadien-1-ones and 4-alkyl-4-cyano- 2,5-cyclohexadien-1-ones,[3,4] the ability to prepare such materials in enantiomerically pure form,[5] the high regioselectivities obtained in the photochemical rearrangements,[2,3] and the qualitative observation that the product bicyclo[3.1.0]hexenones appear to be photo-stable at 366 nm, while they are readily rearranged to phenols at shorter wavelengths.[3] Because the product bicyclo[3.1.0]hexenones are synthetically useful intermediates, the latter observation is of considerable importance. Since this apparent wavelength dependent photo-stability was based on product yields rather than quantum yield data and secondary photochemistry was not rigorously avoided, a quantum yield study of the photochemistry of **1** through **3** was undertaken. The results, of interest both from a synthetic and mechanistic standpoint, are reported below.

All irradiations were conducted on deaerated (N_2) benzene solutions, at less than 4% conversion, using monochromatic light (4 nm bandwidth) and an electronic actinometer calibrated with potassium ferrioxalate actinometry. Product analysis was achieved using standardized capillary gas chromatography.







Irradiation of **1** at both 313 and 366 nm provided **2** and **3** with quantum yields that were independent of irradiation wavelength (Table 1). No phenol **4** was detected until the conversion exceeded 4%, by which time secondary light absorption by **2** and **3** was occurring. Thus, any large change in selectivity between phenol and bicyclohexenone formation with wavelength does not originate from primary photochemistry of **1**, since **2** and **3** are the predominant primary photoproducts.[6]

Irradiation of **2** at 313 nm efficiently afforded epimer **3** (ϕ = 0.2), and phenol **4** (ϕ = 0.3) as primary photoproducts (Table 1). In contrast, irradiation of **2** at 366 nm (Table 1) led to inefficient formation of **3** (ϕ = 0.04) and **4** (ϕ = 0.06), indicating that the photo-stability of **2** is indeed higher at 366 nm than at 313 nm, and confirming the presence of an unusual wavelength dependence that is unprecedented in bicyclo[3.1.0]hexenone photochemistry.

Irradiation of **3** at 313 nm afforded **2**, with ϕ = 0.2, and **4**, with ϕ = 0.1. Irradiation at 366 nm (Table 1) provided **2** (ϕ = 0.2) and **4** (ϕ = 0.04). Interestingly, in contrast to **2**, the quantum yield for epimerization of **3** was wavelength independent, while the quantum yield for phenol formation showed a significant increase at shorter wavelengths. The wavelength dependence in formation of **4** from **3** is similar to that observed from irradiation of 2, but of smaller magnitude.

Noting the UV absorption characteristics of 2 and 3 (2: ϵ_{313nm} = 187, ϵ_{366nm} = 4; and 3: ϵ_{313nm} = 263, ϵ_{366nm} = 12) and the quantum yields indicated in Table 1, the photochemistry obtained with **1** can be summarized. At 313 nm, **2** and **3** are formed initially in a ratio of about 1:2. After light absorption by photoproducts **2** and **3** becomes appreciable, in addition to interconverting with each other, both efficiently rearrange to phenol **4**. At 366 nm, **2** and **3** are again initially formed in a ratio of about 1:2. However, at 366 nm phenol formation is extremely inefficient, and the major secondary photochemistry is epimerization of **3** to give **2**. (Not only is the quantum yield for conversion of **3** to **2** higher than that for conversion of **2** to **3**, but the extinction coefficient of **3** is four times higher than that of **2** at 366 nm.) Thus, after extended irradiation of **1** at 366 nm, the major product obtained is **2** (photostationary ratio of **2** to **3** >9:1[3]). If the reaction is carefully monitored to avoid over irradiation, and stopped at about 95% conversion of **1**, smaller ratios of **2** to **3** can be obtained (ca. 1.5:1). Finally preliminary experiments suggest that triplet sensitization (xanthone) results in an even lower ratio of **2** to **3** (<1:1.3 at 95% conversion).

Table I. Quantum yields for the indicated photochemical transformations at 313 and 366 nm.

	Quantum Yield:[a]	
Transformation:	313 nm	366 nm
1 to **2**	0.09	0.09
1 to **3**	0.2	0.2
2 to **3**	0.2	0.04
2 to **4**	0.3	0.06
3 to **2**	0.2	0.2
3 to **4**	0.1	0.04

[a] estimated error is 10-20%

The observation that photoisomerization of **1** to **2** and **3** occurs equally efficiently at both wavelengths, while **2** and **3** are inefficiently rearranged at 366 nm, definitively establishes the presence of an unusual wavelength dependence and the importance of proper choice of irradiation wavelength for the title rearrangement if isolation of the product bicyclo[3.1.0]hexenones is desired. The wavelength dependence of the photoisomerization between **2** and **3** as well as the transformation of both compounds to **4** suggests that more than one excited state and/or higher vibrational levels of the same state may be involved. The isomerisation between **2** and **3** may be related to the stereochemical relationship of the carbomethoxy group and the enone chromophore. Before more definite mechanistic suggestions can be made, further studies of the substituents on the cyclopropane ring and of the triplet quantum yields must be, and are, being made.

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References and Notes:

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(6) Trace amounts of other minor photoproducts were detected from irradiation of **1** at low conversion but the amount present was too small for quantification in the present study. Preparative irradiation (>300 nm) of **1** in benzene solution gave a 4:1 mixture of the 2-carbomethoxyphenol **4** and the 4-carbomethoxy isomer in 61 % yield. It is noteworthy that **1** gives a mixture of regioisomeric phenols whereas 2,5-cyclohexadienones with a larger 4-alkyl substituent undergo regioselective rearrangement to phenols corresponding to **4** (ref. 3 and unpublished observation of A.G.S.).

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