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Photochemical Rearrangement of 2-Substituted 4-Alkylidene-2,3-epoxy-1-tetralone to 3-(2-Oxoalkylidene)-1-indanone

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Irradiation of 2-substituted 4-alkylidene-2,3-epoxy-1-tetralone results in the rearrangement to 3-(2-oxoalkylidene)-1-indanone or the E-Z isomerization around the double bond. These photoreactions are suggested to occur from the (π,π^*) triplet excited state.

Photochemical reactions of α,β-epoxy ketones have attracted considerable interest from both synthetic and mechanistic standpoints.$^{1,2)}$ Among these, the phototransformations being accepted with maximum attention are the photochemical rearrangement to β-diketones via a homolytic C_α-O bond cleavage and the photochemical generation of carbonyl ylide via a C_α-C_β bond cleavage. The carbonyl ylide thus formed is ultimately trapped by a suitable dienophile or undergoes fragmentation to give carbene and carbonyl compound. However, factors determining the course of photochemical reaction of α,β-epoxy ketones remains uncertain, although they appear to depend on the nature of the excited state and the localization of the excitation energy in the starting molecules.$^{3)}$ In the course of our investigation on the photochemistry of epoxynaphthoquinone,$^{4,5)}$ we have found a novel photorearrangement of methylene analogues of 2-substituted epoxynaphthoquinones, 2-substituted 4-methylidene-2,3-epoxy-1-tetralones (**1**), to 3-alkylidene-1-indanones (**2**).

The title compounds **1a-e** were prepared from of the corresponding 2,3-dihydro-2,3-epoxy-1,4-naphthoquinones by Wittig reaction in moderate yields.[6] Two equivalents of Wittig reagent were necessary to realize a high conversion. Irradiation of a benzene solution of **1a** (0.02 M) with a Pyrex-filtered light from high-pressure Hg lamp under an argon atmosphere for 3 h followed by chromatographic separation on silica gel column furnished a single product **2a** in 44% yield. The IR spectrum of **2a** showed characteristic bands at 1725 cm^{-1} (1-indanone) and 1685 cm^{-1} (a conjugated ketone); the ^1H-NMR spectrum indicated the presence of the acetyl protons at δ 2.37 ppm, the allylic methylene protons at δ 3.65 ppm, and the vinyl proton at δ 6.85 ppm, the latter two protons were coupled mutually with J=2 Hz; the ^{13}C-NMR spectrum revealed the presence of two keto groups at δ 201.7 and 197.4 ppm, the methylene carbons at δ 41.9 ppm, besides eight sp^2 carbons. Further support for the oxoalkylidene indanone structure of **2** came from its ozonolysis to give 1,3-indanedione. Similarly, irradiation of epoxy ketones **1b-e** gave **2b-e** in 27-56% yields (Table 1). Norrish type II products were not observed in the photoreaction of **1d**, although the excitation of the corresponding epoxynaphthoquinone **3** led exclusively to Norrish type II cyclization product **4** via the (n,π^*) triplet state.[4]

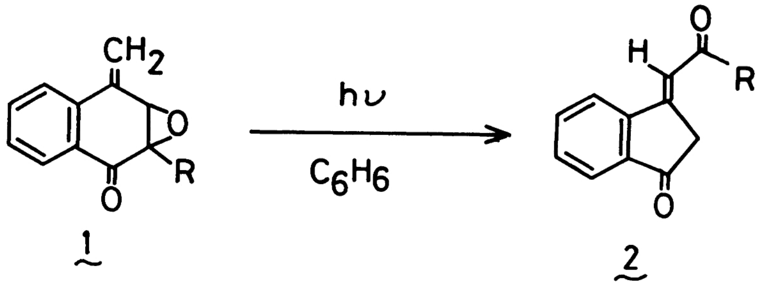
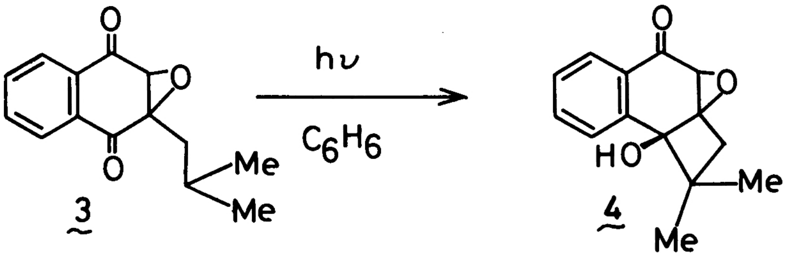


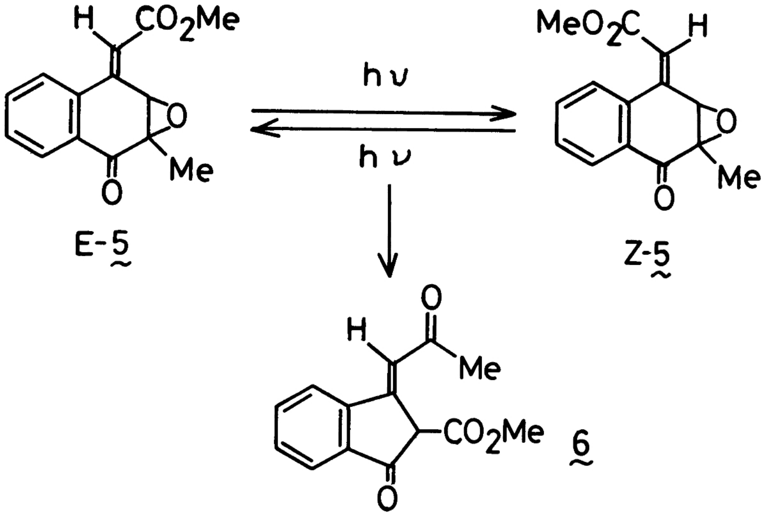
Table 1. Photorearrangement of **1** to **2**

Substrate	R	Irradiation time/h	Conversion %	Photo-product	Isolated yields/%$^{a)}$	Mp $\theta m/^\circ C$
1a	Me	3	80	**2a**	44	147-148
1b	CH_2Ph	19	70	**2b**	33	oil
1c	CH_2OPh	15	83	**2c**	27	125-126
1d	$CH_2CH(Me)_2$	3	73	**2d**	27	73-74
1e	Ph	13	77	**2e**	56	177-178

a) Isolated yields based on the consumed amount of **1**.



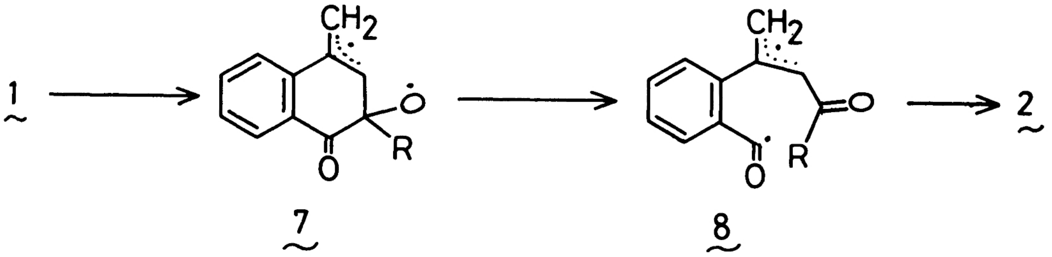
On the other hand, irradiation of α,β-unsaturated esters E-**5** resulted in a smooth isomerization to the Z-**5**. After 30 min irradiation, a photoequilibrated mixture of E- and Z-**5** was formed. However, prolonged irradiation of this mixture produced the indanone **6** in 40% yield.



It was found that xanthone was able to sensitize the photoreactions of **1a**-**e** to give the reaction mixture essentially identical with those obtained upon direct irradiation and that the photoreactions of **1a**-**e** and **5** were efficiently quenched by anthracene, indicating that these photoreaction occurred from their triplet excited state.

In contrast to strong phosphorescence typical of the carbonyl $^{3}(n,\pi^{*})$ excited state of epoxynaphthoquinone **3** (77 K), **1a** and **5** showed no detectable phosphorescence. Lack of Norrish type II products in photoreactions of **1d**, dissimilar to **3**, should be explained in terms of different nature of the electronic state for the lowest triplet state, (n,π^{*}) for **3** and (π,π^{*}) for **1d**. This consideration is supported by the undetectability of phoshorescence in **1a** and **5** and an efficient E-Z photoisomerization of **5**, since $^{3}(\pi,\pi^{*})$ species may cause the very rapid decay via E-Z isomerization prior to phosphorescence.

Accordingly, a plausible mechanism for the formation of **2** and **6** is given in Scheme 1. The photorearrangement would begin with a homolytic C_β-O bond cleavage from the lowest (π,π^*), producing the biradical **7**, which then gives **2** or **6** via the biradical **8**. Postulated C_β-O bond cleavage in **1a-e** and **5a-b** may be brought about as a result of the localization of the excitation energy at the double bond in the triplet excited state of **2** or **6**.



Scheme 1.

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