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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 ^{1}H-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)]

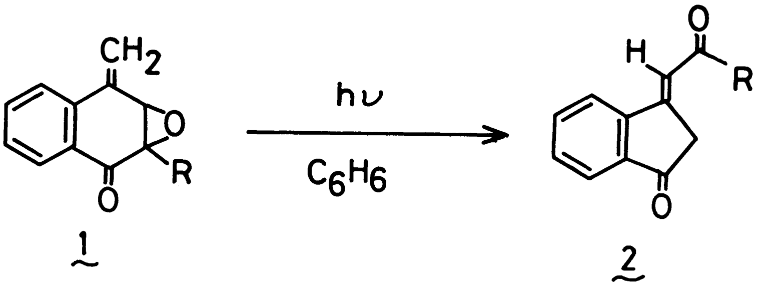
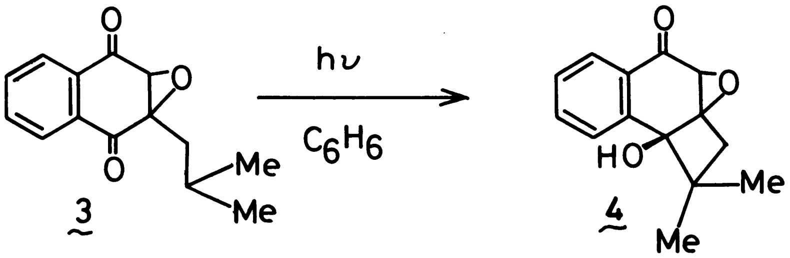


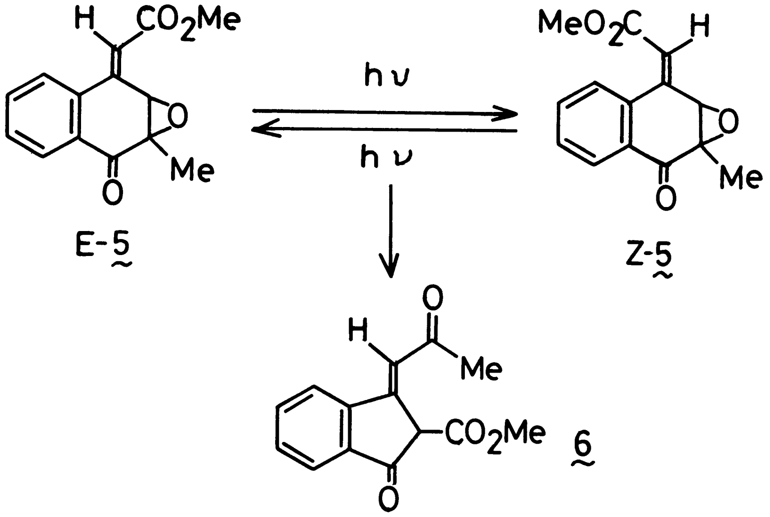
Table 1. Photorearrangement of **1** to **2**

Substrate	R	Irradiation time/h	Conversion %	Photo-product	Isolated yields/%[a)]	Mp θm/°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**.



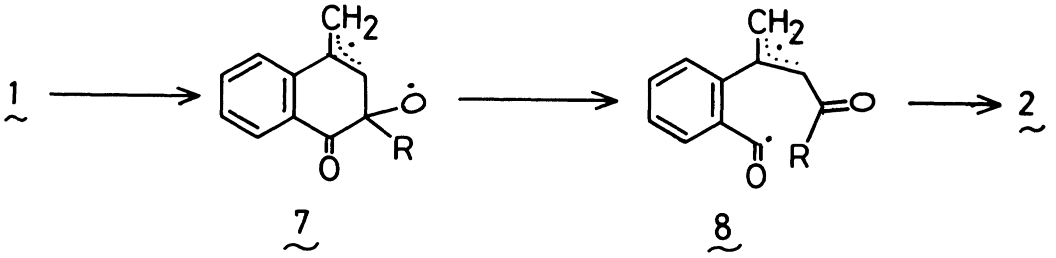
On the other hand, irradiation of α,β-unsaturated esters E-**5** resulted in a smooth isomerization to the Z-**5**. After 30 min irradiation, a photoequilibrated mixture of E- and Z-**5** was formed. However, prolonged irradiation of this mixture produced the indanone **6** in 40% yield.



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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