

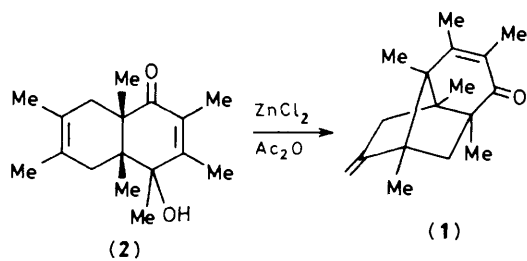
## Photoisomerisation of the Adduct of Bicyclohept-1-en-1-yl and 2,5-Dimethyl-*p*-benzoquinone

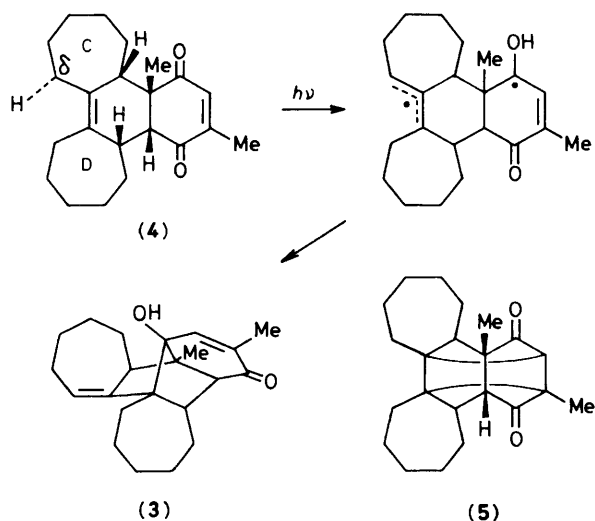
A. Weisz, M. Kaftory, I. Vidavsky, and A. Mandelbaum\*

*Department of Chemistry, Technion—Israel Institute of Technology, Haifa, Israel*

The adduct (**4**) of bicyclohept-1-en-1-yl and 2,5-dimethyl-*p*-benzoquinone on exposure to light isomerizes to the pentacyclic product (**3**) by a long range hydrogen migration which has been previously observed in analogous systems under electron impact.

Jiang *et al.* recently reported the formation of the novel tricyclic system (**1**) by the reaction of the naphthoquinol (**2**) with zinc chloride and acetic anhydride.<sup>1</sup> We report here on the formation of a similar system (**3**) by photoisomerisation of the adduct (**4**) of bicyclohept-1-en-1-yl and 2,5-dimethyl-*p*-benzoquinone.<sup>2</sup> Crystalline (**4**) undergoes an efficient transformation to (**3**) on standing in light (daylight or u.v. radiation). The deterioration of the original crystals is observed after a short time in light, and (**3**) may be easily isolated by flash chromatography on silica gel. This reaction



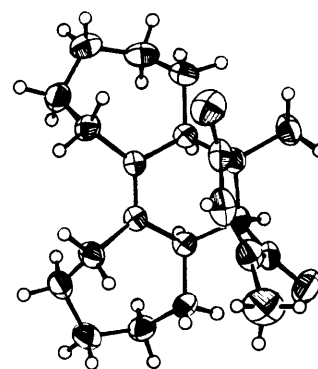


**Table 1.** Distances between  $\delta$ -H and oxygen atoms in adducts (4) with varying size of rings c and d.

Ring size		$\delta$ -H $\cdots$ O distance, Å
c	d	
5	5	3.236
6	5	4.126
6	6	4.820
6	7	3.986
7	7	2.727

also takes place on leaving a benzene solution of (4) in daylight wherein (4) gradually isomerizes to (3). In ethyl acetate this reaction is accompanied by a [2 + 2] addition leading to the cage photoproduct (5). The structural assignments of (3) and (5) have been made by X-ray analyses.

The photoisomerization of (4) to (3) apparently involves migration of an allylic hydrogen atom from a position  $\delta$  to a carbonylic oxygen. A plausible mechanism is shown in Scheme 1. Similar long range hydrogen migrations from  $\delta$ -positions have been observed in this and in other similar systems under electron impact.<sup>3-8</sup> These migrations in the gas-phase radical cations take place to an even greater extent in compounds having smaller c and d rings. The solid state



**Figure 1.** ORTEP representation of adduct (4). Full details of the crystallographic study will be published elsewhere.

photorearrangement described here is limited to both seven membered rings c and d in the adduct (4). A crystallographic study shows that the distance between the  $\delta$ -H atom and the carbonyl oxygen atom is relatively short only in this case (see Table 1 and Figure 1). The adduct of bicyclohept-1-en-1-yl and 1,4-naphthoquinone does not undergo this photorearrangement.

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