

SHORT
COMMUNICATIONS

Photochemical Rearrangement of 3,3,6-Trimethyl-1,5-heptadien-4-one

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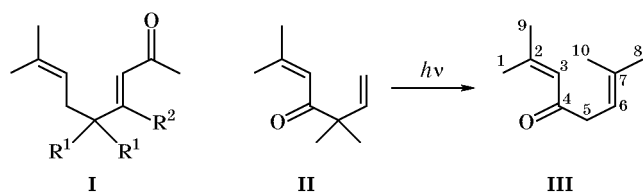
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Received December 20, 2000

We previously examined photochemical reactions of some naturally occurring di- and trienones and their analogs, as well as the effect of complex formation with cyclodextrins on this process [1]. All these ketones had a common structural unit **I** (Scheme 1), and the main transformation was either carbocyclization (in the presence of cyclodextrin) or *cis-trans* isomerization (in the absence of cyclodextrin).

Scheme 1.



R¹, R² = Me or H.

In the present work we have studied photochemical transformations of the natural dienone isolated from *Artemisia* species, 3,3,6-trimethyl-1,5-heptadien-4-one (**II**), which has a different structure of the carbon skeleton: the carbonyl group is located between the double bonds. We have found that irradiation of a solution of ketone **II** results in formation of a single rearrangement product, 2,7-dimethyl-2,6-octadien-4-one (**III**) (Scheme 1).

Let us consider a possible mechanism of this rearrangement. At first glance, it is analogous to that described by us previously [1] for the rearrangement of a series of cyano-substituted dienes, e.g., of nitrile **IV** (Scheme 2). However, a more detailed analysis shows some differences. Obviously, the formation of

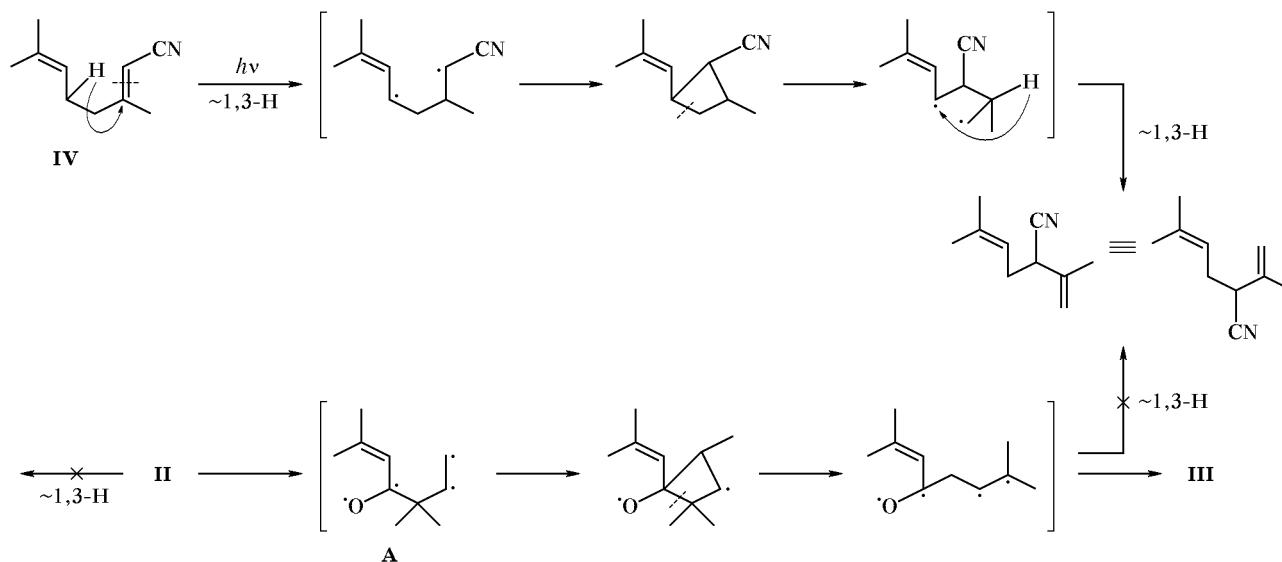
ketone **III** requires generation of two diradical pairs in intermediate **A**, whose further transformations will lead to the final product. In addition, the scheme of transformations of nitrile **IV** includes 1,3-hydrogen shifts which are missing in the reaction sequence leading to ketone **III**. We have found no published data on such a route to ketone **III**. It should also be noted that photochemical reactions of 3,3,6-trimethyl-1,5-heptadien-4-one (**II**) were not studied previously.

The process under study is influenced by both the solvent nature and the presence of cyclodextrin. When ketone **II** was irradiated over a period of 2 h, the fraction of rearrangement product **III** in the mixture was 25% in methanol, 54% in aqueous methanol, 75% in the presence of β -cyclodextrin, and 85% in the presence of α -cyclodextrin (GLC data).

The ¹H and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.13 MHz for ¹H and 100.61 MHz for ¹³C; a 1:1 mixture (by volume) of CCl₄ and CDCl₃ was used as solvent; signals of chloroform were used as reference (δ 7.24 ppm, δ_C 76.90 ppm). The initial compounds and reaction products were analyzed by GLC on a Biokhrom-1 chromatograph equipped with a flame-ionization detector and a 1500 \times 22-mm glass capillary column; stationary phase SE-54; oven temperature 50–200°C; carrier gas helium.

3,3,6-Trimethyl-1,5-heptadien-4-one (**II**) was isolated by vacuum distillation of the essential oil from *Tanacetum vulgare* L. [2]; it was identical to an authentic sample described in [3]. The reaction was carried out under irradiation by a DRSh-1000 lamp over a period of 2 h; the concentration of ketone **II** in methanol and aqueous methanol (1% of MeOH)

Scheme 2.



was 0.1–0.5%. The mixture was separated by column chromatography on silica gel (100–160 μm , Czechia) using gradient elution with pentane–diethyl ether (0 to 10% of the latter). Complexes of ketone **II** with cyclodextrin were prepared and isolated by the procedure described in [1]. The ^1H NMR spectrum of ketone **III** coincided with that reported in [4]. ^{13}C NMR spectrum of **III** (CDCl_3), δ_{C} , ppm: 18.01 q and 20.60 q (C^8 , C^{10}), 25.74 q and 27.57 q (C^1 , C^9), 43.84 t (C^5), 116.91 d (C^6), 123.30 d (C^3), 134.55 s (C^7), 154.27 s (C^2), 197.24 s (C^4).

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