

APPLICATION OF CD MEASUREMENTS TO STEROIDAL ENONE PHOTOCHEMISTRY

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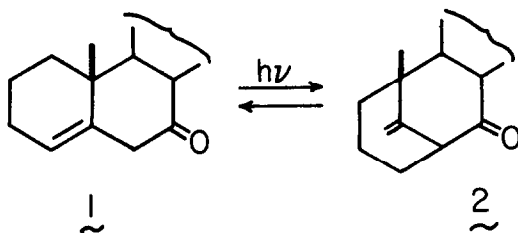
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Difficulties are frequently encountered in quantitative photochemical studies of optically active natural products because the reaction process cannot be followed in a simple manner. This is due to factors such as overlap of substrate and sensitizer/quencher uv absorptions, or insufficient volatility for glc analysis. In the following we report a combined application of cd measurements and monochromatic irradiation to the photochemical studies of β,γ -enones, which in recent years have attracted considerable attention.²⁾

In a previous communication³⁾ we reported that photoirradiation of cholest-4-en-7-one 1 (and related compounds) gave rise to a photoequilibrium mixture with the bridged ketone 2. The nature of excited states of systems such as 1 and 2 cannot be identified readily by conventional methods because of overlap of uv absorptions, i.e., λ_{\max} (EtOH) of 1, 290 nm (ϵ 240) and 2, 290 nm (ϵ 48). The substrates were therefore directly irradiated with a monochrome in a cd cell and the process was followed by measuring the cd curves at suitable time intervals; minute quantities of samples were required because the reaction could be carried out in a single cd cell and because of the large difference in the cd spectra of 1 and 2 (see Figs. 1a and 2a). This enables a photochemical reaction to be followed readily in the presence of large excess amounts of optically inactive quencher and sensitizer, provided that reactant and product have opposite Cotton effect signs.

The substrates were placed in a 1 cm cd cell (4 ml) of the monochromator,⁴⁾ the oxygen was removed by bubbling nitrogen for 30 min, the cell was irradiated



with a monochrome centered at 290 nm, and the cd curves were measured at suitable time intervals. As depicted in Figs. 1a and 2a for the solvent cyclohexane, the extrema of the n, π^* Cotton effects gradually decrease upon irradiation until the same photo-stationary state is attained after ca. 70 min. Similar results were obtained for the solvents dioxane and tert-butanol.

The quantum yields were estimated by measuring concentrations from cd curves, converting these to uv ϵ values at 290 nm, and using the first order equation: $\ln(e^{2,303\epsilon cd} - 1) = -2.303\epsilon I_0 \phi$. The data employed for calculations were only those for the early stage of the reaction, during which absorption of the product was weak. The light intensity was measured with a ferrioxalate actinometer. The quantum yields thus calculated for conversions of isomers 1 and 2 in cyclohexane at 290 nm, respectively, were roughly 0.1 and 0.3.

The change in cd curves were unaffected when photoisomerizations were carried out in the presence of a 100-fold excess of t-piperylene (E_T 57 kcal/mole). For example, the quantum yields of isomerizations of 1 and 2 after addition of t-piperylene remained unchanged and were 0.1 and 0.3 respectively (Figs. 1b and 2b).

The isomerizations of 1 and 2 were not sensitized with acetophenone (E_T 74 kcal/mole) upon irradiation at 360 nm; this was clear from cd curves which underwent no change.

Fig. 1a (cyclohexane)
 (enone 1) = 1.7 mmol/l

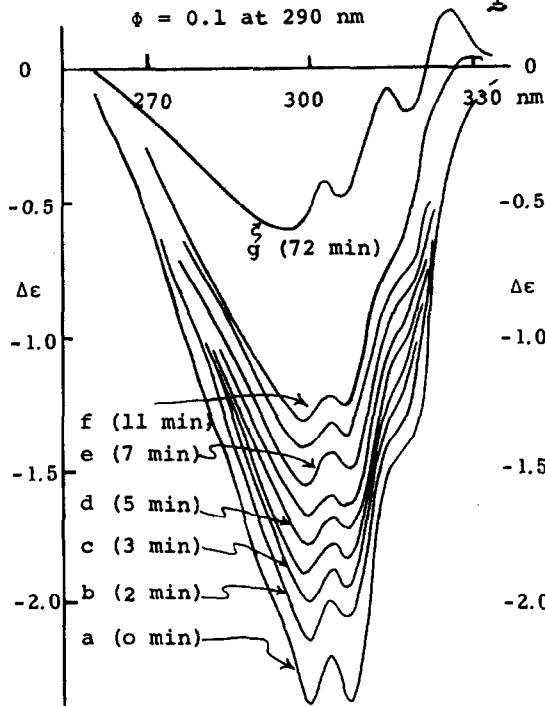
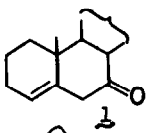


Fig. 1b (cyclohexane)
 (enone 1) = 1.66 mmol/l
 (piperylene) = 0.213 mol/l

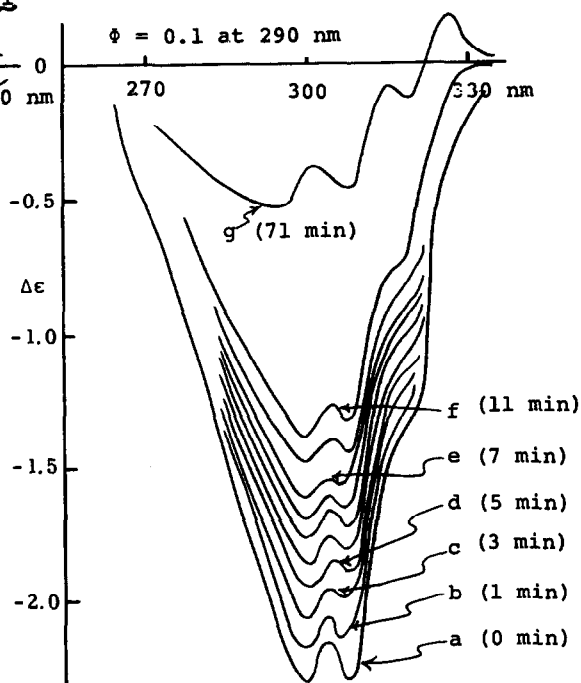


Fig. 2a (cyclohexane)
 (enone 2) = 9.07 mmol/l

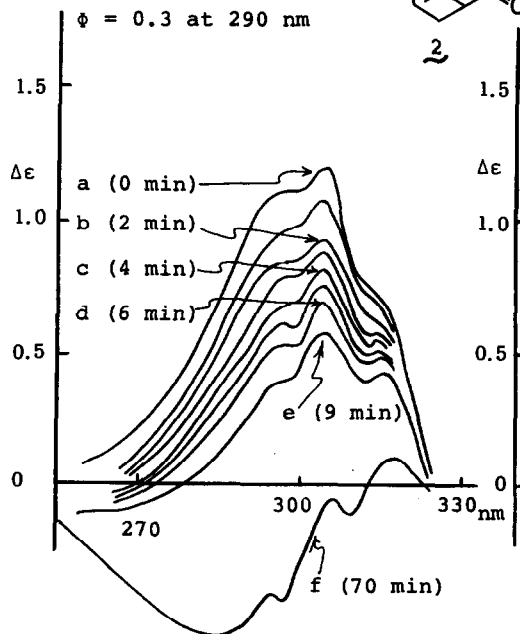
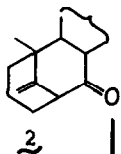
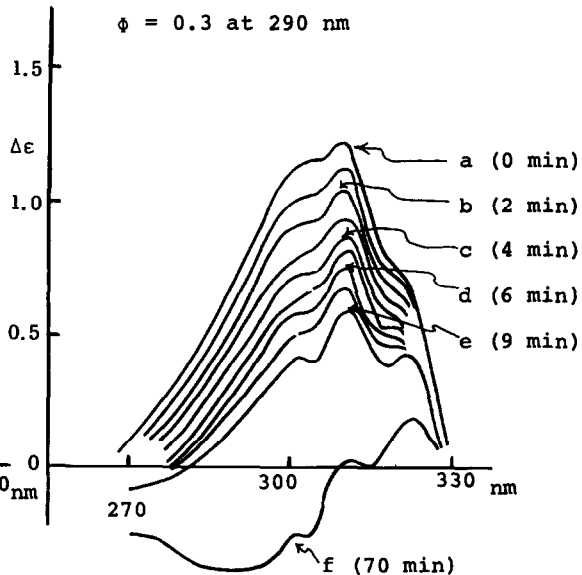
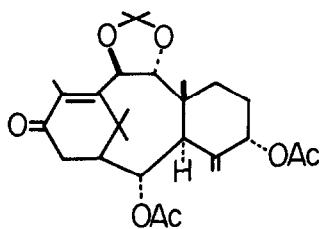


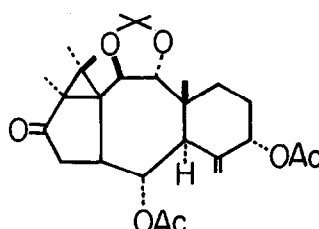
Fig. 2b (in cyclohexane)
 (enone 2) = 1.87 mmol/l
 (piperylene) = 0.275 mol/l



Application of the present method to the acetophenone sensitized photo-reaction of taxinine derivative 3 leading to 4 showed in a clear manner that an efficient triplet reaction had taken place.⁵⁾ In numerous other cases where optically active natural products are involved, the present method would substantially simplify photochemical studies.



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- 4) A JASCO CRM-FA instrument was employed for monochromatic irradiations; we are grateful to the Japan Spectroscopic Company, Hachioji, Tokyo, Japan, for loan of the CRM instrument.
- 5) T. Kobayashi, M. Kurono, H. Sato, and K. Nakanishi, submitted for publication in *J. Amer. Chem. Soc.*