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A New Photoextrusion Reaction of a Cyclohexa-2,5-dienone

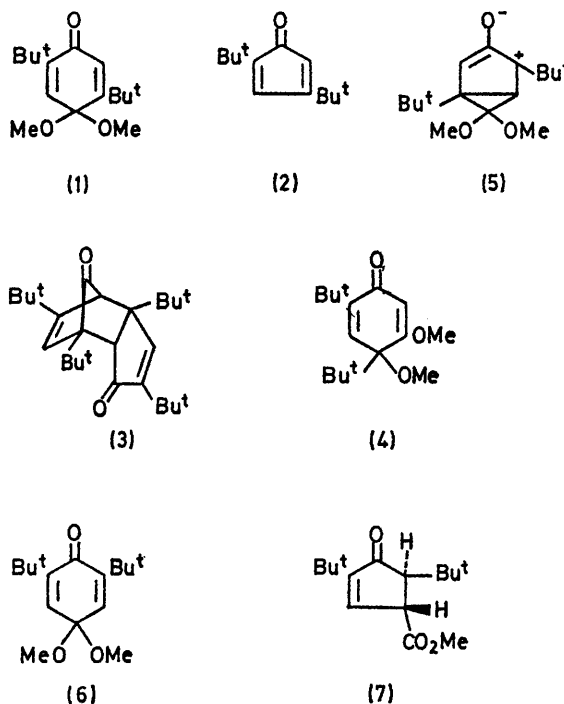
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Summary A new type of photoproduct, a cyclopentadienone formed by an unprecedented photoextrusion process, has been isolated from the photolysis of a cyclohexa-2,5-dienone.

MANY different products are formed from the irradiation of cyclohexa-2,5-dienones.¹ All may be produced through transient bicyclohexane zwitterions² which are stabilised by rearrangement to other cyclohexadienones, bicyclohexenones, or cyclopentenones each of which may be further phototransformed.³ All of the cyclohexa-2,5-dienones which have been investigated to date have had at least one alkyl or aryl substituent in the 4-position. Here we describe an unprecedented photoreaction of a dienone having two oxygen substituents at the 4-position, *viz.*, 4,4-dimethoxy-2,5-di-*t*-butylcyclohexa-2,5-dienone (**1**).⁴

The ketone (**1**) (1.80 g) in benzene (300 ml) was irradiated through Pyrex glass with visible light for 20 h or with light of wavelength 366 nm for 5 h. Chromatography of the crude product over silica gel (Merck HF₂₅₄) gave two identified components. The faster moving was 2,4-di-*t*-butylcyclopentadienone (**2**) (0.50 g, 38%), obtained as a yellow oil which decolourised during 15 h at room temperature and was converted into the dimer (**3**), ‡ m.p. 151–152° (lit.⁵ 151–152°). The second product was 4,5-dimethoxy-2,4-di-*t*-butylcyclohexa-2,5-dienone (**4**) ‡ (0.50 g, 28%) [m.p. 79–80°; ν_{\max} (Nujol) 1650, 1625 (C=O), 1600 cm⁻¹ (C=C); n.m.r. δ (CCl₄) 0.93, 1.23 (2 × Bu^t), 3.08, 3.76



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‡ A satisfactory elemental analysis was obtained for this compound.

(2 × OMe), 5.48, 6.30 (2 × =CH); λ_{\max} (MeOH) 291, 241 nm (log ϵ 3.54, 4.06); further characterised by zinc-acetic acid reduction to the known⁶ 5-methoxy-2,4-di-*t*-butylphenol]. Two other products of this reaction are still under investigation.

Although the cyclohexadienone (4) represents a common class of photorearrangement product, cyclopentadienone formation has not previously been reported. The product (2) might arise by a concerted cheletropic elimination of dimethoxycarbene from either the dienone (1) or the zwitterion (5) (or its triplet precursor). Analogous thermally induced eliminations are known.⁷ To date we have been unable to identify the extruded fragment.

To test the generality of the process we irradiated the

isomeric dienone (6)⁴ under similar conditions. No cyclopentadienone was formed. Instead the product was the ester (7)⁸ (60%) [oil; ν_{\max} (film) 1680, 1715 cm^{-1} (C=O); n.m.r. δ (CCl_4) 0.97, 1.17 (2 × Bu^t), 2.47 (d, J 3 Hz, CH), 3.38 (t, J 3 Hz, CH), 3.70 (CO_2Me), 7.02 (d, J 3 Hz, =CH)] which was hydrolysed by sodium hydroxide in aqueous methanol to the corresponding acid[†] [m.p. 129–130°; ν_{\max} (Nujol) 2500–3300 (OH), 1700 cm^{-1} (C=O); n.m.r. δ (CCl_4) 1.00, 1.18 (2 × Bu^t), 2.48 (d, J 3 Hz, CH), 3.42 (t, J 3 Hz, CH), 7.03 (d, J 3 Hz, =CH), 12.03 (CO_2H)].

We are unable to rationalise adequately the divergent behaviour of the cyclohexadienones (1) and (6) at present.

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¹ D. A. Plank, J. C. Floyd, and W. H. Starnes, jun., *Chem. Comm.*, 1969, 1003.

² H. E. Zimmerman, *Adv. Photochem.*, 1963, **1**, 183.

³ D. A. Plank and J. C. Floyd, *Tetrahedron Letters*, 1971, 4811.

⁴ D. G. Hewitt, *J. Chem. Soc. (C)*, 1971, 2967. The dienones (1) and (6) are most conveniently prepared by treatment of a methanolic solution of 4-methoxy-2,5- or -2,6-di-*t*-butylphenol with a molar equivalent of *N*-bromosuccinimide in the presence of excess of sodium bicarbonate (*cf.* W. Dürckheimer and L. A. Cohen, *Biochemistry*, 1964, **3**, 1948).

⁵ The spectroscopic properties of both the cyclopentadienone (2) and its dimer (3) were in complete agreement with those reported by E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, 1969, **91**, 6785.

⁶ C. J. R. Adderley and F. R. Hewgill, *J. Chem. Soc. (C)*, 1968, 1438.

⁷ R. W. Hoffman and J. Schneider, *Tetrahedron Letters*, 1967, 4347.

⁸ The *trans*-stereochemistry shown for the cyclopentenone (7) was assigned from the n.m.r. coupling constants using the Karplus equation (L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd edn., Pergamon, Braunschweig, 1969, p. 280). The n.m.r. spectra are very similar to those of closely related photoproducts reported elsewhere (E. R. Altwick and C. D. Cook, *J. Org. Chem.*, 1964, **29**, 3087; T. Matsuura and K. Ogura, *J. Amer. Chem. Soc.*, 1967, **89**, 3850) to which the same stereochemistry has been assigned.