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

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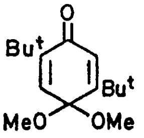
Summary A new type of photoproduct, a cyclopentadienone formed by an unprecedented photoextrusion process, has been isolated from the photolysis of a cyclohexa-2,5-dienone.

Many different products are formed from the irradiation of cyclohexa-2,5-dienones.[1] All may be produced through transient bicyclohexane zwitterions[2] 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 HF_{254}) 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 (CCl_4) 0·93, 1·23 (2 × Bu^t), 3·08, 3·76



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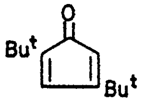

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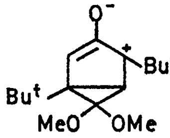

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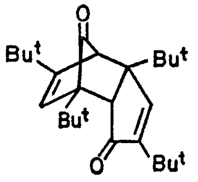

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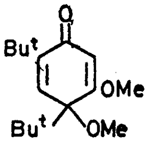

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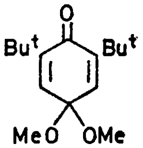

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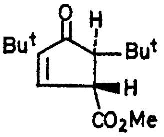

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‡ A satisfactory elemental analysis was obtained for this compound.

(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 known[6] 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 cheleotropic 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, C*H*), 3·38 (t, *J* 3 Hz, C*H*), 3·70 (CO_2Me), 7·02 (d, *J* 3 Hz, =C*H*)] 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, C*H*), 3·42 (t, *J* 3 Hz, C*H*), 7·03 (d, *J* 3 Hz, =C*H*), 12·03 (CO_2*H*)].

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. Altwicker 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.