Mass-spectrometric Approach to the Determination of the Structure of the Product from Irradiation of 2,5-Dimethyl-3,4-diphenylcyclopentadiene Dimer

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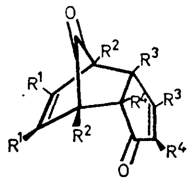
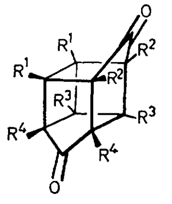
Summary The symmetric irradiation product of 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (**1**) was proven by mass spectrometry to have the structure (**3**), of symmetry C_{2v}; a new technique for the preparation of β-deuteriated ketones is described.

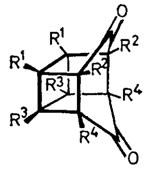
The major product from irradiation of the dissociating dimer (**1**) of 2,5-dimethyl-3,4-diphenylcyclopentadienone has been shown to exhibit improper symmetry [in contrast to the minor, disymmetric cage product (**2**)],[1] and there are two possibilities, (**3**) and (**4**), of symmetry C_{2v} and D_{2h}, respectively, for its structure. However, no adequate chemical (or physical) method has been found to distinguish between these possibilities, owing to the complete inertness of this high melting (m.p. 272), insoluble compound towards a wide variety of chemical reagents.[1]



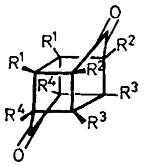
(1)



(2)



(3)

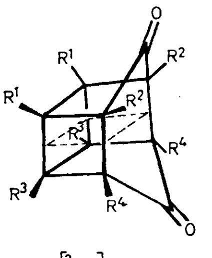


(4)

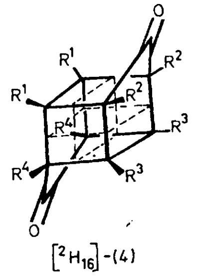
Non-deuteriated compounds: $R^1 = R^3 = C_6H_5$; $R^2 = R^4 = CH_3$

[$^2H_{32}$]-compounds: $R^1 = R^3 = C_6D_5$; $R^2 = R^4 = CD_3$

[$^2H_{16}$]-compounds: $R^1 = C_6H_5, R^2 = CH_3; R^3 = C_6D_5, R^4 = CD_3$
or $R^1 = C_6D_5, R^2 = CD_3, R^3 = C_6H_5, R^4 = CH_3$



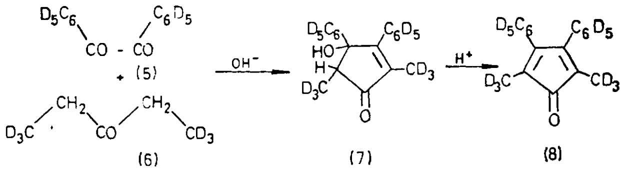
[$^2H_{16}$]-(3)



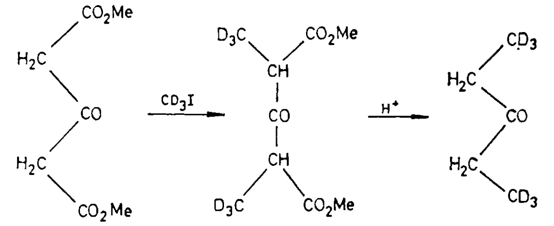
[$^2H_{16}$]-(4)

We present herein the proof that the correct structure is in fact (**3**), using mass spectrometry in conjunction with deuterium labelling.

The approach was based on the observation that the most abundant ion in the mass spectrum of the compound under investigation is $M^+/2$ (*m/e* 260), *i.e.* the cage fragments into its two cyclopentadienone halves. Hence, if all four substituents of only half of the molecule could be labelled, *e.g.* perdeuteriation of only one dimethyldiphenylcyclopentadienone unit, the choice would be between [$^2H_{16}$]-(**3**) and [$^2H_{16}$]-(**4**). However, the $M^+/2$ fragments of [$^2H_{16}$]-(**3**) would consist (see Scheme) in *m/e* 260 and 276 ions whereas [$^2H_{16}$]-(**4**) would have two statistically equal probable fragmentation modes available: one yielding also *m/e* 260 and 276 and the other *m/e* 266 and 270 ions.



(1)



(2)

$$[^2H_{32}]\text{-}(1) + (1) \rightleftharpoons [^2H_{16}]\text{-}(1) \xrightarrow{h\nu} (3) + [^2H_{16}]\text{-}(3) + [^2H_{32}]\text{-}(3)$$

+ the analogous substituted derivatives of (2)

(3)

The labelled compound [$^2H_{32}$]-(**1**) was synthesized along the lines of the original procedure[2] for preparation of (**1**) [equation (1)]. [$^2H_{10}$]Benzil (**5**) was obtained from [$^2H_5$]-benzaldehyde (Merck) in a well documented sequence of reactions.[3] [$^2H_6$]Diethyl ketone (**6**) had been prepared previously,[4] but by a cumbersome and expensive procedure, and we used the sequence in equation (2); dimethoxycarbonylacetone was dialkylated with CD_3I (Miles–Yeda) and the product underwent acid hydrolysis–decarboxylation to (**6**) in 64% overall yield. We are elaborating this procedure to a more general method for preparation of β-deuteriated ketones, and [$^2H_3$]ethyl methyl ketone has been prepared in an analogous manner from acetylacetone.

Base-catalysed condensation of compound (**5**) with compound (**6**) followed by acid-catalysed dehydration of (**7**) yielded the perdeuterio-compound (**8**) [equation (1)], which undergoes reversible dimerization to [$^2H_{32}$]-(**1**). Subsequently [equation (3)], a benzene solution of a mixture of [$^2H_{32}$]-(**1**) with an equimolar quantity of (**1**) was refluxed to yield a chemically pure product which is actually a statistical mixture of (**1**), [$^2H_{16}$]-(**1**), and [$^2H_{32}$]-(**1**) in the ratio 1 : 2 : 1 as seen from the mass spectrum which shows molecular ions at *m/e* 520, 536, and 552 in this ratio.

Irradiation of this isotopic mixture at $\lambda > 300$ nm gave a minute quantity of the disymmetric cage product, m.p. 318 °C, along with the major product, m.p. 272 °C.[1] The mass spectrum of the latter molecular ions at *m/e* 520, 536, and 552 in the same ratio as above and the $M^+/2$ fragment ions at *m/e* 260 and 276. No ions at *m/e* 266 and 270 were recorded. Thus, structure (**3**) is unequivocally proven.

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[1] (a) B. Fuchs, B. Pazhenchevsky, and M. Pasternak, *Tetrahedron Letters*, 1972, 3051; (b) B. Fuchs, *J. Amer. Chem. Soc.*, 1971, **93**, 2544.

[2] C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, 1942, **64**, 1260; 1950, **72**, 5165.

[3] *Org. Synth.*, 1941, Coll. vol. **1**, 87, 94.

[4] L. C. Leitsch and A. T. Morse, *Canad. J. Chem.*, 1953, **31**, 785.