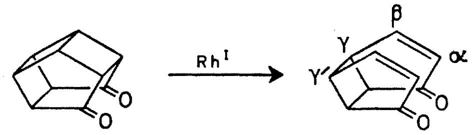
Rhodium(I)-catalysed Isomerization of Cyclobutane Cage Compounds: Synthesis of *cis,syn,cis*-Tricyclo[5,3,0,$0^{2,6}$]deca-4,8-diene-3,10-dione and of *exo*-Dicyclopentadienone

By PHILIP E. EATON* and STEVEN A. CEREFICE

(*Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois* 60637)

Summary *cis,syn,cis*-Tricyclo[5,3,0,$0^{2,6}$]deca-4,8-diene-3,10-dione has been synthesized and shown to rearrange photochemically to *exo*-dicyclopentadienone.

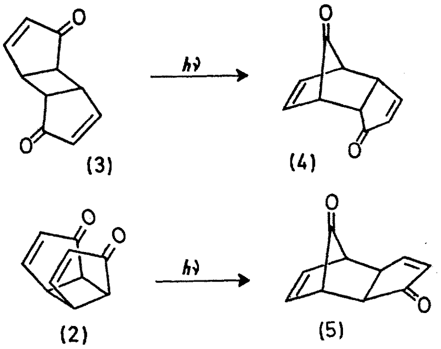
THE extraordinary ability of rhodium(I) complexes to effect cyclobutane → diolefin cleavage in the cubane system was reported recently.[1] Other less strained systems containing a number of cyclobutane rings fused seriatim are also subject to such transformations, sometimes in a very useful way. We report here that the cage diketone (**1**), available in moderate yield by the method of Pettit and his co-workers,[2] is isomerized quantitatively to a new



(1) (2)

compound by a catalytic amount of [Rh(norbornadiene)-$Cl]_2$ or $[Rh(CO)_2Cl]_2$ in chloroform solution at 65°.† The reaction product, m.p. 148—149°, has been assigned structure (**2**) by consideration of its origins and from spectroscopic data: i.r. ν ($CHCl_3$) 1720 (C=O) and 1580 cm^{-1} (C=C); n.m.r. δ ($CDCl_3$) 7·41 (H_β, 2H, d of t, $J_{\alpha\beta}$ 5·6 Hz, $J' = \frac{1}{2}|J_{\beta\gamma} + J_{\beta\gamma'}|$ = 1·4 Hz), 6·40 (H_α, 2H, d, J 5·6 Hz), 3·9 (2H, m), and 3·3 p.p.m. (2H, m). The carbon skeleton of (**2**) is quite well-known, but only in the *cis,anti,cis*-configuration; such compounds are prepared for the most part using photocycloaddition reactions of cyclopentenes.[3] Members of the *cis,syn,cis*-series are less common; (**2**) appears to be the first certain compound in this series unsubstituted at the bridgehead positions.

As reported in the preceding communication,[4] irradiation of the *cis,anti,cis*-compound (**3**) gives, *via* internal rearrangement, *endo*-dicyclopentadienone (**4**). Similar irradiation‡ of the *cis,syn,cis*-isomer (**2**) gives in 90% yield, presumably *via* an analogous route,§ the previously unknown *exo*-isomer (**5**) of dicyclopentadienone, m.p. 81—82°. The identification of (**5**) follows unambiguously from the spectral data: i.r. ν (CCl_4) 1790 (bridge C=O), 1720 (conjugated C=O), and 1590 cm^{-1} (conjugated C=C); n.m.r. δ (CCl_4) 7·54 (H_β, 1H, d of d, J 5·8, 2·4 Hz), 6·80 (2H, m), 6·22 (H_α, 1H, d of d, J 5·8, 1·5 Hz), 3·2—2·8 (3H, m), and 2·37 (1H, d, J 6·8 Hz).



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† As we shall discuss in a future paper, the direction of ring opening in such reactions is dependent on the electronic nature of substituent groups.

‡ In benzene solution using light of wavelengths > 3000 Å. Some (*ca.* 10%) of (**2**) is converted into (**1**) under these conditions.

§ Cyclopentadienone cannot be an intermediate in the conversion of (**2**) into (**5**) as its dimerization gives exclusively *endo*-dicyclopentadienone.

[1] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515.

[2] J. C. Barborak, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 1328.

[3] P. E. Eaton, *J. Amer. Chem. Soc.*, 1962, **84**, 2344, 2454; J. R. Scheffer and B. A. Boire, *Tetrahedron Letters*, 1969, 4005; J. R. Scheffer and M. L. Lungle, *ibid.*, p. 845.

[4] P. E. Eaton and T. W. Cole, jun., preceding communication.