A New Heterocyclic Cage Ring System: Preparation of the *cis*-Cyclobutane Dimer of Dibenzo[*a*,*d*]cyclohepten-5-one

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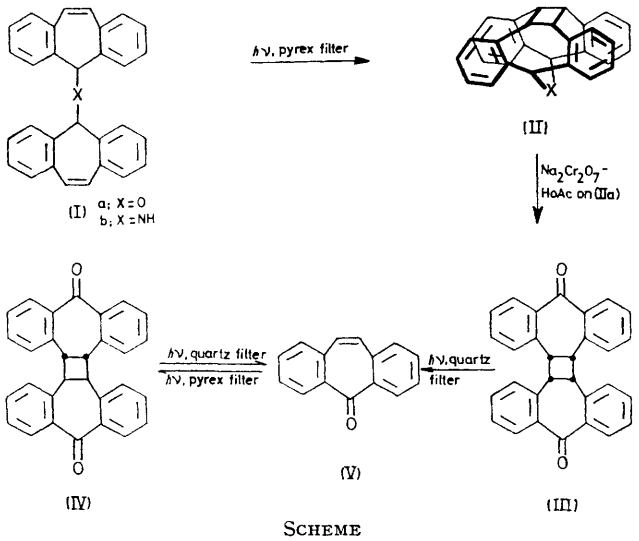
Summary The photochemical synthesis of a new heterocyclic cage ring system is described, which provides a route to the previously unknown *cis*-cyclobutane dimer of the dibenzo[*a*,*d*]cycloheptene ring system.

KOPECKY and SHIELDS have reported[1] the photochemical dimerization of dibenzo[*a*,*d*]cyclohepten-5-one, which yielded exclusively the *trans*-cyclobutane dimer (IV) (Scheme). We now report the preparation of the *cis*-cyclobutane dimer through a novel heterocyclic ring cage system.

Irradiation of bis(dibenzo[*a*,*d*]cycloheptene) 5-oxide, (Ia),[2] (10 g) in benzene solution (2—5%) with a 450 W Hanovia high pressure lamp with a pyrex filter until the starting material had disappeared (t.l.c.), gave, after evaporation of the solvent to dryness and chromatography on silica gel, a 70% yield of the new cyclobutane cage compound, 2,3:6,7:9,10:13,14-tetrabenzo-15-oxatetracyclo[6.6.1.$0^{4,12}$.$0^{5,11}$]-pentadecane, (IIa), m.p. 213 °C. Recrystallization from benzene (1:1 benzene solvate) did not improve the melting point. The n.m.r. spectrum shows the disappearance of the olefinic protons of (Ia) and the appearance of a singlet (4H) at δ 4·9. The u.v. spectrum shows one band [λ(EtOH) 215 nm (ϵ 4·62)], characteristic of the saturated tricyclic system. Analysis and the chemical ionization spectrum ($M^+ + 1$, *m/e* 399) confirmed the identity of the compound.

Oxidation of the cage ether (IIa) with $Na_2Cr_2O_7$ in acetic acid gave the *cis*-diketone (III) in 65% yield, m.p. 239—242 °C (benzene). The n.m.r. spectrum ($CDCl_3$), [δ 4·83 (4H, s, cyclobutane) 7—7·9 (16H, m, aromatics)] and mass spectrum (M^+ 412) confirm the identity of the compound. The corresponding n.m.r. data for the *trans*-diketone (IV) are δ 4·13 (s, cyclobutane) and 7—7·9 (m, aromatics). The *cis*-isomer is significantly less soluble in organic solvents than the *trans* and is easily distinguished from the latter by t.l.c. Although the m.p. is coincidentally the same as the *trans*-isomer, the mixed melting point is depressed (226—242 °C). Comparison of the u.v. and i.r. spectra of the *cis*- [λ (EtOH) 218 (ϵ 4·62), 266 nm (4·46); $\nu_{C=O}^{KBr}$ 1640 cm^{-1}] and *trans* [λ (EtOH) 219 (ϵ 4·58), 267 nm (4·37); $\nu_{C=O}^{KBr}$ 1660 cm^{-1}] ketones does not indicate the presence of

any special intramolecular interactions in the former compound.



SCHEME

Final proof of structure was obtained when irradiation of the *cis*-, (III), and *trans*-, (IV), isomers in dilute acetonitrile or ether with a 200 W Hanovia high pressure lamp using a quartz filter (> 200 nm) for an hour afforded quantitatively the dibenzo[*a*,*d*]cycloheptene-5-one, (V), which was identical in both cases with an authentic sample of the ketone, by i.r., m.p. and mixed m.p.

It was of interest to extend the preparation of the same ring system to include other heteroatoms such as nitrogen. Bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amine, (Ib), could be prepared in 80% yield by stirring a mixture of 5-chloro- and 5-amino-dibenzo[*a*,*d*]cycloheptene in ether in the presence of triethylamine, m.p. 167–169 °C (EtOH). The u.v. spectrum shows the typical absorption for the 10,11-unsaturated tricyclic system, λ (EtOH) 215 (ε 4·74), 287 nm (4·41).

The n.m.r. spectrum of this compound shows an interesting pattern. In [$^2H_6$]-Me_2SO the 5,5′ hydrogens appear as four sets of doublets which on D_2O exchange collapse to 4 singlets of approximately equal intensity (δ 3·42, 4·11, 4·58, and 4·93). The 10,11 and 10′,11′ olefinic protons show two sharp and one broad singlets (δ 6·78, 6·98, and 7·02). A variable temperature study shows that on warming the 5,5′ protons gradually collapse and at 170°C a sharp singlet is obtained (δ 4·40, 2H). There is a concomitant collapse of the olefinic bands to a sharp singlet (δ 6·88, 4H). On cooling the original spectrum is restored.

Tochtermann *et al.*[3] have shown in a similar n.m.r. temperature study that in dibenzo[*a*,*d*]cyclohepten-5-one dimethylacetal the doublet for the two methyls collapses into a singlet at 100°C and that this was due to slow flipping of the seven-membered ring. In our case, slow flipping of the two seven-membered rings in (Ib) should give rise to three conformers in equilibrium: axial–axial, axial–equatorial, and equatorial–equatorial. These three conformers would be predicted to give rise to four peaks in the n.m.r. spectrum for the 5,5′ hydrogens. The fact that four peaks of approximately equal intensity are observed indicates that there is a significant amount of each conformer present, although a more detailed assignment cannot be made at present.

Irradiation of a suspension of (Ib) (10 g) in 350 ml of benzene under the conditions previously described, for 18 h, yielded, on filtration, 5·1 g of an isomeric amine, m.p. 242–244 °C. The u.v. spectrum, as in the case of the cage ether, shows one band, λ (EtOH) 208 nm (ε 4·46). The n.m.r. spectrum (CF_3CO_2D) shows the cyclobutane protons at δ4·9 (4H, s), the protons α to the nitrogen at 5·9 (2H, br s) and the aromatics at 6·8—7·8 (16H, m). The mass spectrum shows the correct molecular ion at M^+ 397. By analogy with the behaviour of (Ia), and the physical data reported, the cage structure (IIb) is assigned to the product.

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[1] J. Kopecky and J. E. Shields, *Tetrahedron Letters*, 1968, **24**, 2821; *Coll. Czech. Chem. Comm.*, 1971, **36**, 3517.
[2] G. Becti, *Gazzetta*, 1957, **87**, 293.
[3] W. Tochtermann, V. Walter, and A. Mannschreck, *Tetrahedron Letters*, 1964, **40**, 2981.