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A NEW ROUTE TO 1,2 : 7,8-DIBENZOCYCLONONATETRAENE VIA AN ELECTROCYCLIC REACTION OF 2,3 : 5,6-DIBENZOBICYCLO[5.2.0]NON-8-ENE

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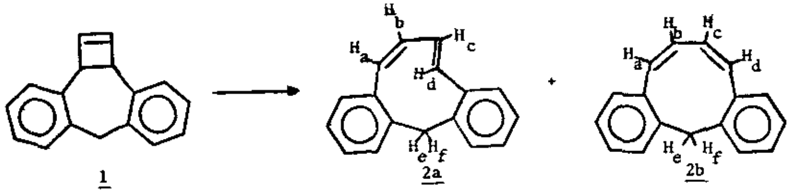
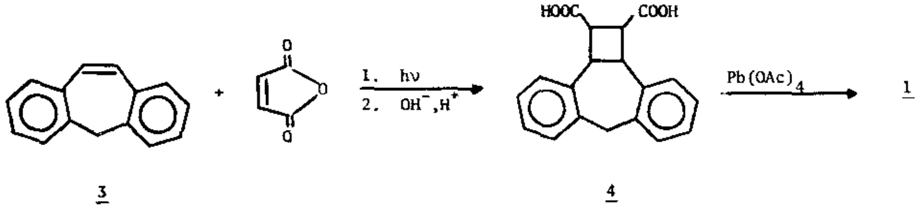
3,4 : 5,6-Dibenzocyclononatetraene[1] and 1,2 : 5,6-dibenzocyclononatetraene[2] have previously been prepared. We wish to report the synthesis of 2,3 : 5,6-dibenzobicyclo[5.2.0]non-8-ene 1 and its conversion via a valence isomerization[3] to *cis,trans*-1,2 : 7,8-dibenzocyclononatetraene 2a. This electrocyclic reaction proceeds in a conrotatory fashion. The *cis,cis*-isomer 2b is obtained by further thermal isomerization. Compounds 2a and 2b are the only members of the dibenzocyclononatetraene series containing a butadiene bridge.

Irradiation of 2,3 : 6,7-dibenzocycloheptatriene 3 and maleic anhydride (Hanovia 450W) using benzil as sensitizer and followed by basic hydrolysis yielded the diacid 4 (70%)[4]; m/e 308 (M), 290 (M - H_2O), 192 (100%); ν_{max}^{nujol} (cm^{-1}) 1700 (C=O). Oxidative bisdecarboxylation with lead tetraacetate[5] yielded 1 (23%)[4] m.p. 70°; m/e 219, 218 (M, 100%).

At the probe temperature (+33°) the ^1H nmr of 1 showed the following parameters: δ ppm ($CDCl_3$) 4.02 (broad, 2H, methylene), 4.54 (s, 2H, benzylic), 6.45 (broad, 2H, vinylic), 7.00-7.35 (m, 8H, arom.). This spectrum was temperature dependent. At -30°, a new pattern appeared, assigned to two boat conformers in a ratio of 2 : 1 $\Delta G^{*}_{+8^\circ} = 14.1$ and 13.7 $\frac{\text{Kcal}}{\text{mole}}$ respectively.

Thermolysis of 1 was effected by passing a benzene solution of 1 through a glass chip filled 20 cm glass tube at 290°. A mixture of three products was obtained (column





chromatography - silica): cis,trans-1,2 : 7,8-dibenzocyclononatetraene 2a (19%)[4], cis,cis-1,2 : 7,8-dibenzocyclononatetraene 2b (14%)[4,7]. Both 2a and 2b showed the same mass spectrum, m/e 219, 218 (M, 100%). Analyses of the ^{1}H nmr spectra of 2a and 2b were based on their high resolution spectra at 300 MHz[6c] and the assignments were confirmed by double resonance experiments.[6c]

The following pmr parameters were observed for 2a[6c], δ ppm ($CDCl_3$) =3.46 (d, 1H, J=14 Hz, H_f), 4.24 (d, 1H, J=14 Hz, H_e), 5.95 (ddd, 1H, J_1=16, J_2=2.5, J_3=1 Hz, H_c), 6.15 (dd, 1H, J_1=16, J_2= 1 Hz, H_d), 6.46 (ddd, 1H, J_1=11, J_2=2.5, J_3=1 Hz, H_b), 6.60 (dd, 1H, J_1=11, J_2=1Hz, H_a), 7.00-7.28 (m, 8H, arom.). The pmr spectrum of 2b[6c] is as follows: δ ppm ($CDCl_3$) = 4.38 (s, 2H, He, H_f), 5.89 (d, 2H, J=12 Hz, H_b, H_c), 6.23 (d, 2H, J = 12 Hz, H_a, H_d) 6.95-7.15 (m, 8H, arom.). The coupling constants of the vinylic protons strictly confirm the assigned configurations of 2a and 2b. Gradual increase of the thermolysis temperature effected concomitant disappearance of 2a whose disappearance was faster than that of 2b. At the same time, a new compound appeared.[8] On the basis of the thermal behaviour of 1 we conclude that the electrocyclic ring opening of 1 to 2a proceeds according to the Woodward-Hoffman rules.[9] This is the first isolable cis,trans-cyclononatetraene derivative.[10] In turn 2a is thermally isomerized to 2b, the all cis isomer. It should be noted that when cyclobutene rings fused to dibenzannelated-five and -six membered rings were thermally isomerized to the corresponding dibenzannelated-cycloheptadiene and -cyclooctadiene systems, only an all cis bridge was identified.[3] A similar mechanism has been proposed for the thermal rearrangement of 9-methylbicyclo[6.1.0]nonatriene.[11]

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References and Notes

1. a) P. J. Garratt and K. A. Knapp, J.C.S.Chem.Comm., 1215 (1970); b) M. Rabinovitz, A. Gazit and E. D. Bergmann, ibid., 1430 (1970).
2. M. Rabinovitz and I. Willner, Tetrahedron Letters, 4447 (1974).
3. a) Cf. J. Meinwald, G.E. Samuelson and M. Ikeda, J.Amer.Chem.Soc., 92, 7604 (1970); b) E. Vogel, W. Frass and J. Wolpers., Angew. Chem., 75, 979 (1963); c) I. Willner and M.Rabinovitz, Tetrahedron Letters, 1223 (1976).
4. All new compounds gave satisfactory C,H analyses.
5. C. A. Grob, M. Ohta, E. Renk and A. Weiss, Helv. Chim. Acta 41, 1191 (1958).
6. a) In ppm downfield from Me_4Si; b) Varian HA-100D spectrometer. For decoupling a Hewlett-Packard 4204A oscillator was used; c) Varian SC-300 PFT spectrometer; d) Bruker HFX-90 PFT spectrometer.
7. A third compound, viz. 3, originating from partial cycloreversion of 1, was observed.
8. Thermolysis at 400° yielded solely a new compound identified as trans fused dibenzobicyclo-[5.2.0]non-8-ene (60% yield[4], m.p. 54° m/e 218 (M). Catalytic hydrogenation (pd/C 10%) reduced the cyclobutene double bond (m/e = 220).
9. R. B. Woodward and R.Hoffman, "The Conservation of Orbital Symmetry", Verlag Chemie, Academic Press, Inc., Weinheim/Bergstr.
10. Only the U. V. spectrum of trans,cis[3] cyclononatetraene has been reported. Cf. S. Masamune, K. Hojo, G. Bigam and D. L. Rabenstein, J. Amer. Chem. Soc., 93, 4966 (1971).
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