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TRIS-[2.2.1]- and TRIS-[2.2.2]-σ-HOMOBENZENES

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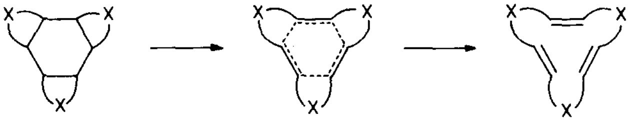
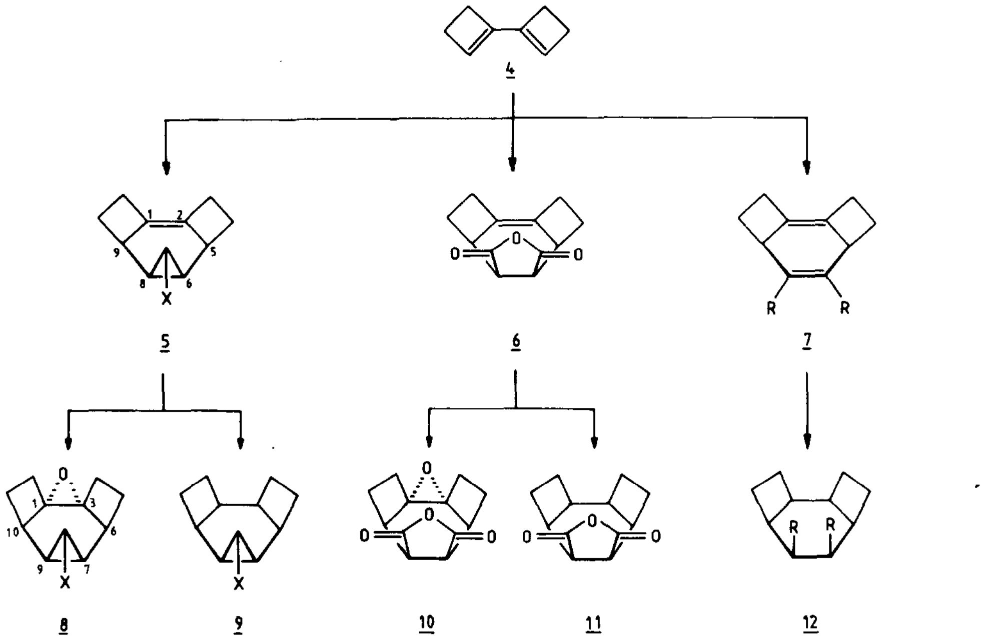
Abstract: Tris-[2.2.1]- and tris-[2.2.2]-σ-homobenzenes are synthesised by reaction of 1,1'-bicyclobutenyl with appropriate dienophiles and hydrogenation of the adducts.

For [2+2+2]-cycloreversions of the type 1 → 3, the "homoaromatic" stabilisation of the transition states 2 is very much dependent on the length of the bridges (X). In the case of the [1.1.1]- as well as the [2.1.1]-framework, this process is thermally favoured and occurs still more readily for the cis- than for the trans-geometry [1]. The sterically determined limits of the "homoaromaticity" for this process (selectivity, stereochemistry) should be attained by means of the [2.2.1]- and [2.2.2]-homologues with their 11- and 12-membered transition states resp. In view of the considerable activity in the area of cyclobutabenzenes [2,3] involving very similar synthetic operations, we report here our preliminary results, in so far as they are based on the 1,1'-bicyclobutenyl described by Heinrich and Lüttke [4,5].



1 2 3

Although 4 in THF/pentane solution (2h, sealed tube, 60°C) failed to react with cyclopropene to give 5a, it readily cycloadds 3-cyanocyclopropene [6]; according to TLC and ^{1}H-NMR spectroscopy the addition takes place stereospecifically. 5b is isolated as colourless prisms (m.p. 71.5-73°C, m/e = 171 (M^+)) in a not yet optimised yield of 65% and is assigned the cis-geometry from $(J_{6,5}+J_{6,9}) = (J_{8,9}+J_{8,5}) \simeq 5$ Hz (determined from a high field ^{1}H-NMR spectrum in $[d_6]$-benzene) [8] and from the interplanar angle of 40° or 105° for *cis*- or *trans*-geometry resp. 5b is cleanly hydrogenated with Pd/C (20°C) or diimine to give 9b (colourless prisms, m.p. 59-60.5°C) 8). A complete ^{1}H-NMR analysis 8) was possible using the epoxide 8b (m.p. 150-151.5°C, m/e = 187 (M^+)), which is prepared by *m*-chloroperbenzoic acid oxidation of 5b (69%) and possesses a similar boat-shape (H(6)-C-C-H(7) 45° (*cis*) or 120° (*trans*) resp.).

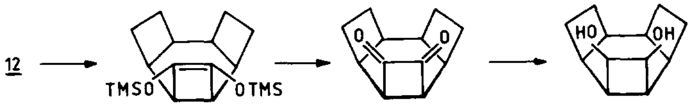


a : X = H b : X = CN c : $X = CO_2CH_3$ $R = CO_2CH_3$

The set of coupling constants confirms the *cis*-geometry. In the same way as cyanocyclopropene, although somewhat slower, the corresponding carbomethoxycyclopropene 9) was converted into the liquid product 5c (4h, 50-60°C, CCl_4).

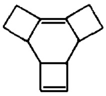
4 reacts with maleic anhydride only in the presence of catalytic amounts of $CuCl_2$ in THF (50-60°C); although the yield of isolated adduct (colourless plates, m.p. 56-57°C, m/e = 204 (M^+)) is so far only moderate (35-40%), no further adduct is to be found. For the adduct 6 $(J_{6,5}+J_{6,8}) = (J_{7,8}+J_{7,5}) = 9.5$ Hz was determined 8). Hydrogenation over Pd/C (20°C, ethyl acetate) quantitatively produces 11 as colourless crystals 8). With an interplanar angle of 10° or 145° for the epoxide 10 or the *trans*-isomer resp., the *cis*-geometry is evident from $(J_{7,6}+J_{7,9}) = (J_{8,9}+J_{8.6}) \simeq 10$ Hz 8).

Esterification with methanol (c. H_2SO_4, 65°C) gives the diester 12 as a colourless oil (65-70%) [8]. Using standard conditions [10] 12 is converted into olefin derivative 13 and that in turn to the diketone 14 and the diol 15.



13 14 15

7 is obtained cleanly and in high yield from 4 and dimethyl acetylenedicarboxylate [2] and its hydrogenation is being investigated as a source of the 12-15 analogues for the *trans*-series; via cyclopropanation or oxidation of the ester-substituted double bond, 7 or the 1,2-dihydrocompound provide entry into activated [2.2.1]-systems [1]. Cyclobutadiene reacts with 4 (EtOH, 2-3h, room temp.); however, to date, it has not been possible to isolate the adduct 16, a potential precursor of 17, a key [2.2.2]-σ-homobenzene.



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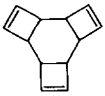

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2) K.G. Bilyard, P.J. Garratt, A.J. Underwood, R. Zahler, Tetrahedron Lett. 1979, 1815; cit. lit.

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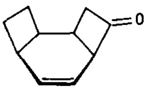
4) F. Heinrich, W. Lüttke, Liebigs Ann. Chem. 1978, 1880; we thank Prof. Lüttke for a copy of his manuscript describing 4 prior to publication.

5) Parallel to this work, *cis*-/*trans*-[2.2.1]- and [2.2.2]-derivatives are being

approached via the [2.2]-ketones i and ii (H. Prinzbach, H.-P. Schal, D. Hunkler, Tetrahedron Lett. 1978, 2195; I.M. Takakis, W.-C. Agosta, ibid. 1978, 531).



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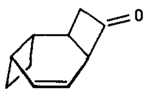

ii

6) T. Tsuchiya, H. Arai, H. Igeta, Chem. Commun. 1972, 1059; here generated by gas-phase pyrolysis (400°C) of dimethyl 3-*anti*-cyano-*exo*-tricyclo[$3.2.2.0^{2,4}$]nona-6,8-diene-6,7-dicarboxylate 7).

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8) 5b (360 MHz, [d_6]-benzene):δ = 1.05 (t, J = 5 Hz, 7-H); 1.30 (m, 6-,8-H); 1.38 (m), 1.85 (m) (4-,10-H); 2.18 (m), 2.32 (m) (3-,11-H); 2.80 (m, 5-,9-H). 6 (360 MHz, $CDCl_3$):δ =2.35 (m), 2.55-2.75 (m) (3-,4-,9-,10-H); 3.12 (m, 5-,8-H); 3.35 (m, 6-,7-H). 8b (360 MHz, $CDCl_3$):δ = 1.11 (t, J = 5 Hz, 8-H); 1.49 (m),2.32 (m) (5-,11-H); 1.81 (m, 7-,9-H); 2.13 (m), 2.51 (m) (4-,12-H); 2.96 (m, 6-,10-H); $J_{4,4}$ = 13.5; $J_{4,5}$ = 4, 8.5, 9.5, 11; $J_{4,6}$ = 1.5; $J_{5,5}$ = 11.5; $J_{5,6}$ = 7.5, 10; ($J_{7,6}+J_{7,10}$) = 6.5-7; $J_{7,8}$ = 5.5 Hz. 9b (360 MHz, $CDCl_3$):δ = 1.67-1.95 (m, 9H, inc. δ1.73 (7-H), 1.83 (6-,8-H)); 2.34 (m, 2H); 2.6 (m, 4H). 10 (360 MHz, $CDCl_3$) :δ = 1.63 (m), 2.22 (m) (5-,10-H); 2.14 (m), 2.50 (m) (4-,11-H); 3.20 (m, 6-,9-H); 3.27 (m, 7-,8-H). 11 (250 MHz, $CDCl_3$):δ = 1.90 (m), 2.15 (m) (3-,4-,9-,10-H); 2.61 (m, 1-,2-H); 2.95 (m, 5-,8-H); 3.21 (m, 6-,7-H). 12 (360 MHz, $CDCl_3$): δ = 1.85 (m), 2.01 (m) (3-,10-H); 2.17 (m, 4-,9-H); 2.60 (m, 1-,2-H); 2.96 (m, 5-, 8-H); 3.03 (m, 6-,7-H); 3.68 (s, OCH_3).

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