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CIS - AND TRANS-DIOXA-TRIS-$[2.1.1]$-σ-HOMOBENZENES

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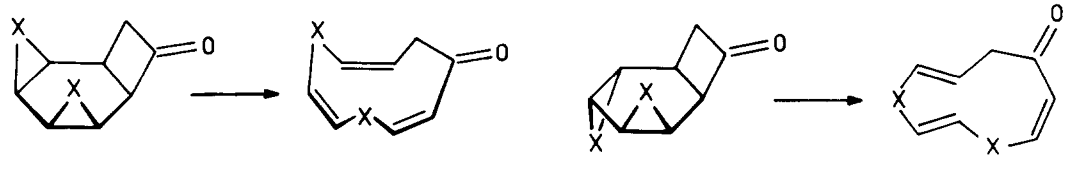
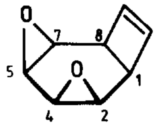
Abstract: The three dioxa-tris-$[2.1.1]$-σ-homobenzenes (5)-(7) have been synthesised. Preliminary thermolysis experiments in the gas-phase (350-400°C) allow a qualitative description of their thermal isomerisation processes.

We recently showed, that for the carbocyclic tris-$[2.1.1]$-σ-homobenzenes (1)/(3) (X=CH_2) the dis,dis,dis - and dis,con,con-$[\sigma 2+\sigma 2+\sigma 2]$-cycloreversion, resp., to Z,Z,Z-(2) and E,E,Z-cyclodecatrienone (4), resp., is clearly the kinetically favoured, thermal stabilisation process 1). Whether the heterocyclic $[2.1.1]$-analogues (X=O,NTos) similarly undergo a specific and stereoselective $[\sigma 2+\sigma 2+\sigma 2]$-cycloreversion, for which the activation barrier is expected to be about 20-40 kJ·mol^{-1} higher 2), is of theoretical and preparative interest 3). Here we describe the synthesis of the isomeric dioxa-tris-$[2.1.1]$-σ-homobenzenes (5)-(7) as potential precursors of the oxa- and aza-frameworks. For the sterically "pretentious" (5) the reaction sequence (8)→(9)→(10a) →(10b)→(11a)→(11b)→(12)→(5) is, despite a number of limitations, a practicable approach, which makes use of (10a), a compound first prepared by *Kitahara et al.* 4) through $^1O_2$-addition to (8) and LAH-reduction of (9). The critical *cis*-hydroxylation step to give (11a) is not yet optimised; the bis-mesylate (10b) does react rapidly with $KMnO_4$ at -15°C (acetone) but the product, which precipitates with a preparative yield of round 80%, consists of an approx. 65:35 mixture of 3β,4β-(11a) and 3α,4α-diol (11a'). To date it has not been possible to separate this mixture, which, after quantitative conversion into the diacetates (11b)/(11b'), can be dehalogenated with Zn/I_2 in DMSO to (12) in 30% (possibly improvable) yield. The considerable material loss



(1) (2) (3) (4)



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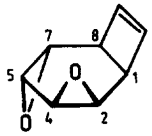

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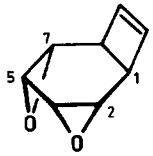
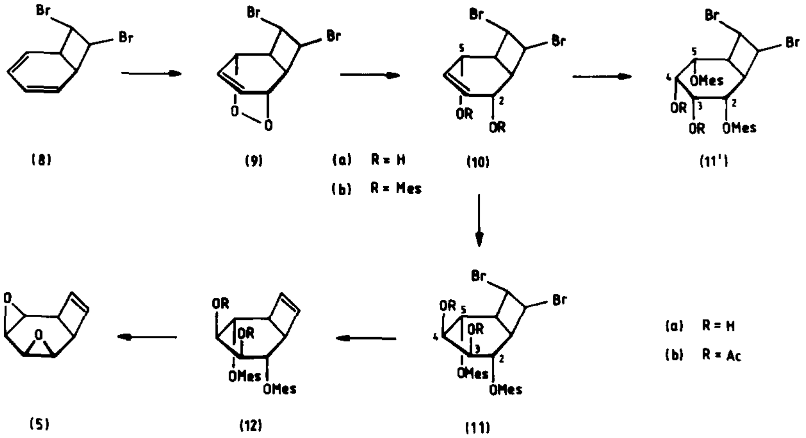
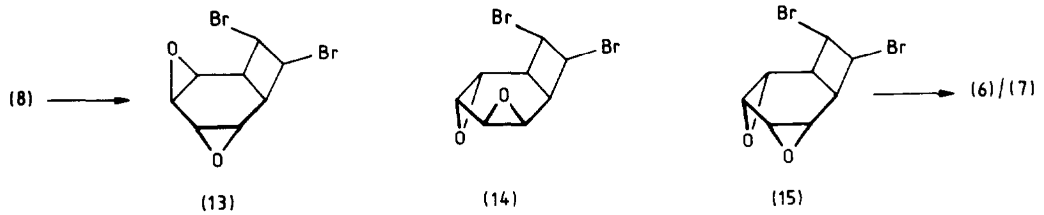


(7)

during the double epoxide formation with 5% methanolic KOH solution (20°C, 25 min) was less expected (present yield 40%). It cannot be excluded, that the proximity of the cyclobutene C=C double bond and the nucleophilic centres leads to side reactions. In accord with the ^{1}H-NMR spectroscopic assignment of (11a), the all-cis-configuration of crystalline (5) (m.p. 66°C) is endorsed by the appropriate ring coupling: $J_{1,2} = J_{7,8} = 4.0$ Hz. With m-chloroperbenzoic acid (m-CPBA) (CH_2Cl_2, 20°) (5) is stereospecifically epoxidised, whereby the 9α,11α-configuration is provisionally preferred (m.p. 138-139°C).

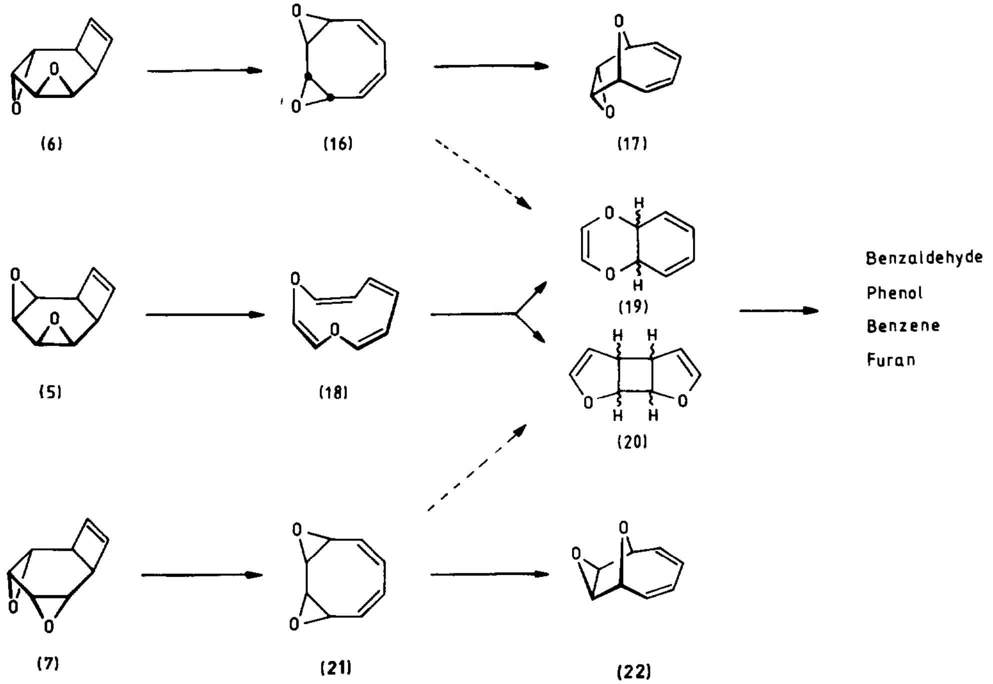


(8) also serves as a precursor of (6) and (7). After two-fold and practically quantitative epoxidation (3 equiv. m-CPBA, 10-20°C)[5] the three diepoxides (13)/(14) (40%, m.p. 79-80°C; 10%, m.p. 108°C) and the known (15)[4,7] (45%) are isolated by column chromatography (SiO_2, CH_2Cl_2/CCl_4 1:1). Upon dehalogenation (Zn/I_2, DMSO)(13) and (14), separately or as a mixture, yield the very low melting (m.p.26°C, 70%), unsymmetrical (6). The symmetrical (7) (m.p. 114°C, 75%) is obtainable from (15). (7), however, is available more efficiently by the almost uniform photolysis (high pressure mercury lamp, pyrex, acetone) of the endo-peroxide (9)[8] followed by dehalogenation (75%). In contrast to (5), (6) and (7) cannot be epoxidised stereospecifically; in each instance a mixture (5:3 and 17:3, resp.) is formed and the NMR assignment of the individual components is not unequivocal. The coupling constants, $J_{1,2} = 5.0$, $J_{4,5} = 1.5$ and $J_{7,8} \sim 0$ Hz, and $|J_{1,2}+J_{1,7}| \sim 0$ Hz, are again typical for the proposed arrangement of the small rings around the basic 6-membered ring in (6) and (7), resp.



In view of the unstability of the potential [σ2+σ2+σ2]-cycloreversion products

(1,4-dioxacyclodeca-2,5,7,9-tetraenes (e.g. (18)) under the thermolysis conditions, no specific, mechanistic information could be expected. A number of observations pertaining to the gas-phase thermolyses (contact time approx. 0.1 sec) and pertinent for the ketones (1)/(3) are reported here: (5) is stable up to 300°C; at 340°C (approx. 60% conversion), the decomposition products, benzene (3%), phenol (13%), benzaldehyde (13%) and furan (6%), are obtained, together with a non-identified (polymeric) fraction. From (6) and (7), with comparable conversion (400°C), however with reduced polymer formation, the same decomposition products (benzene 11% and 15%,resp., benzaldehyde 7% (8%), phenol 7% (8%) and furan 3% (2%)) are produced but the major product is (17) (22%) and (22) (17%, m.p. 52°C), resp., an isomerisation product in each case. Based on comparisons with related isomeric <u>cis</u>- and <u>trans</u>- tris-σ-homobenzenes and annelated cyclobutenes[10)], one possible explanation of these results is,



that (5) undergoes the $[\sigma2+\sigma2+\sigma2]$-cycloreversion to (18), which affords the decomposition products via (19) and (20). In the case of (6) and (7) the cyclobutene ⟶ butadiene opening to (16) and (21), resp., is likely to be the first step. <u>Anastassiou et al.</u>[11)] have already shown, that at 200°C (16) is converted into (17).

The new compounds have been fully characterised (elemental analysis, ^{1}H-, ^{13}C-NMR, MS). Selected ^{1}H-NMR-data (C_6D_6, 360 MHz) are presented: (5) δ= 5.80 (9(10)-H), 2.80 (4(5)-H), 2.60 (2(7)-H), 2.54 (1(8)-H); (6):δ = 6.01 (10-H), 5.88 (9-H), 3.23 (5-H), 3.15 (4-H), 3.07 (8-H), 3.03 (7-H), 3.00 (2-H), 2.88 (1-H); (7): δ = 5.59 (9(10)-H),2.95 (1(8)-H), 2.83, 2.59 (4(5)-, 2(7)-H); (22) ($CDCl_3$): δ = 6.01 (2(5)-H), 5.93 (3(4)-H), 4.71 (1(6)-H), 3.75 (7(9)-H).

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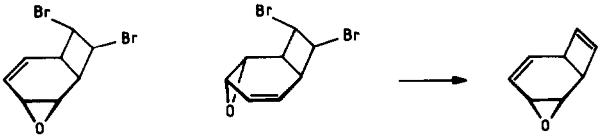
1) H. Prinzbach, H.-P. Schal, D. Hunkler, H. Fritz, Angew. Chem. 92, 575 (1980); Angew. Chem. Int. Ed. Engl. 19, 567 (1980).

2) G. McMullen, G. Sedelmeier, R. Hildebrand, H. Fritz, H. Prinzbach, Tetrahedron Lett. 1979, 3847; H. Prinzbach, H.-P. Schal, D. Hunkler, Tetrahedron Lett. 1978, 2195.

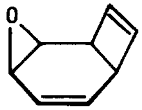
3) R. Schwesinger, M. Breuninger, B. Gallenkamp, K.-H. Müller, D. Hunkler, H. Prinzbach, Chem. Ber. in press.

4) M. Oda, Y. Kayama, Y. Kitahara, Tetrahedron Lett. 1974, 2019.

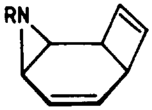
5) Monoepoxides (A) and (B) are selectively formed with one equiv. of peracid at 0°C [6] and from them (C) is obtainable. Using well-tried procedures, the cis-bis-[2.1]-σ-homobenzenes (D)-(F) were prepared from (A)-(C). (D) and (E) undergo [π2+σ2+σ2]-cycloreversion at 170°C (H. Prinzbach, M. Maas, W. Marterer, in preparation).



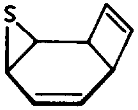
(A) (B) (C)



(D)



(E)



(F)

6) M. Oda, M. Oda, Y. Kitahara, Tetrahedron Lett. 1976, 839.

7) W. Adam, M. Balci, Tetrahedron 36, 833 (1980).

8) The more laborious synthesis of (7) from the endo-peroxide (^{1}H-NMR($CDCl_3$): δ=6.30 (9(10)-H), 6.02 (3(4)-H), 4.83 (1(6)-H), 3.03 (2(5)-H)) of the thermally labile bicyclo[4.2.0]octa-2,4,7-triene [9] has also been realised.

9) E. Vogel, M. Kiefer, W.R. Roth, Angew. Chem. 76, 432 (1964); Angew. Chem. Int. Ed. Engl. 3, 442 (1964).

10) G.R. Branton, H.M. Frey, R.F. Skinner, Trans. Farad. Soc. 62, 1546 (1966); R. Criegee, Angew. Chem. 80, 585 (1968); Angew. Chem. Int. Ed. Engl. 7, 559 (1968).

11) A.G. Anastassiou, E. Reichmanis, J. Org. Chem. 38, 2421 (1973).

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