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Bis-[2.X]-σ-HOMOBENZENES 1)

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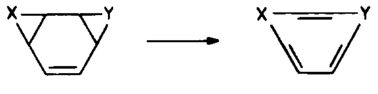
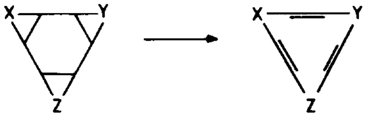
The geometry of the cis-bis-(1) and cis-tris-σ-homobenzenes (2) is unusually favourable for their [2s+2s+2s]-cycloreversion. For that reason, it is argued, the "homoaromatic" stabilisation in their homobenzenoid transition states is remarkable even in cases with relatively unfavourable three-membered-ring components X, Y, Z (e.g. oxygen) 2). An obvious test for this argument is the successive replacement of the three-membered rings in (1) and (2) by cyclobutane rings as in the series (3) to (7) 3). For the cyclobutane ring it is known, from examples with probably much less favourable stereoelectronic prerequisites, that participation in co-operative processes is much less efficient because of the strongly diminished bent-bond character 4). In addition to this mechanistic aspect we are interested in the systems (3)-(7) for synthetic purposes.



(1)



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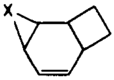
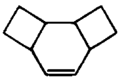


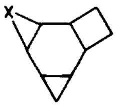
Bis - [2.1]

(3)



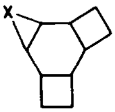
-[2.2]

(4)



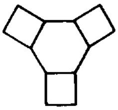
Tris - [2.1.1]

(5)



-[2.2.1]

(6)



-[2.2.2]

(7)

The communication from Takakis and Agosta 5) prompted us to report some of our efforts in the series (3) to (7), specifically the application of photochemical 1,3-acyl migrations 6) in the tricyclic ketones (8)/(12) 7) for the synthesis of the cis / trans-bis-[2.X]-σ-homobenzene-ketones (10a)/(10b) and (14a)/(14b). It should be emphasised, that at this preliminary stage, the detailed analysis of the nature and relative rates of competing and of consecutive reactions (e.g. reversion, decarbonylation, ketene- elimination, dimerisation) and of their wavelength-dependance has not yet been pursued. The results of our direct irradiation of (8a) (15 mmol, 350 cc ether, falling film irradiation apparatus, Hanau TQ 150 lamp, quarz vessel, control by vpc, tlc (SiO_2, CH_2Cl_2/ether)) are comparable to those in l.c. 5); after 55 % conversion the trans-[2.1]-ketone (10a) is formed in ca. 50 % yield. Under the same conditions (55 % conversion) (8b) yields the trans-[2.2]-ketone (10b) (liq.) in up to 75 % yield. Probably for stereoelectronic reasons the photolysis of (12a) 8) seems to be more selective than in the case of (8a); after approx. 80 % conversion - there is very little (11a) and no evidence of [2π+2σ]-competition 9) - the cis-[2.1]-ketone (14a) amounts to 70-75 % (liq.; 2,4-dinitrophenylhydrazone m.p. 110°C). At the same conversion (80 %) (14b) (liq.; 2,4-dinitrophenylhydrazone m.p. 105°C), however, is obtained from (12b) in only 30-40 % yield; in a still speculative argument the higher steric strain in (14b) is responsible.

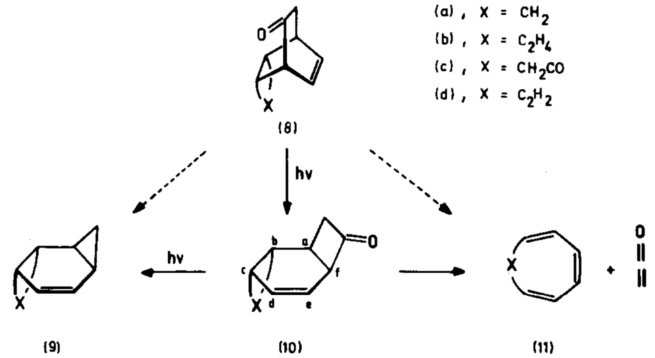
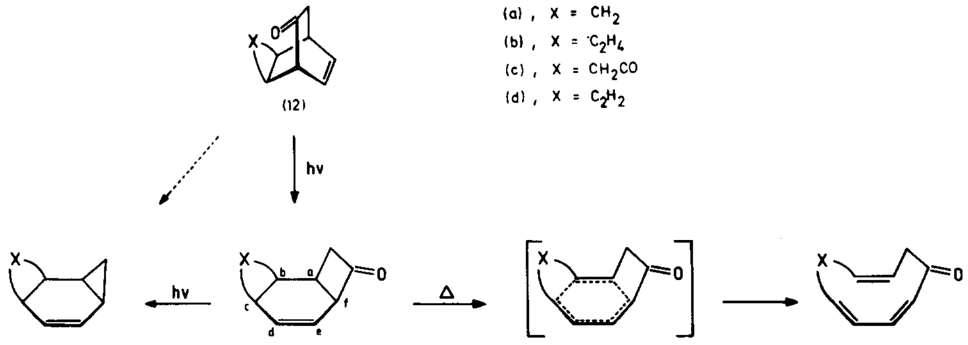


Table: ^{1}H-nmr data (360 MHz, $CDCl_3$) of (10a)/(10b) and (14a)/(14b)

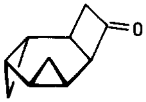
	δ(ppm)							J(Hz)					
	a	b	c	d	e	f		ab	bc	cd	de	ef	fa
(10a)	3.01	1.38	1.32	6.18	5.21	3.42	3.18,3.12,1.06, 0.38	0	8.5	5	10.5	4.5	9.5
(10b)	2.46	1.98	2.76	5.87	5.69	3.61	2.93,2.83,2.71, 2.20,1.80,1.43,	0	8	3.0	10.0	5	8
(14a)	2.75	1.64	1.43	6.33	5.50	3.85	3.44,2.91,0.93, 0.05	7	8	5.0	10.0	6.0	9.5
(14b)	2.51	2.94	2.67	5.87	5.81	3.72	3.14,2.59,2.11, 1.84,1.72,1.40	8	9	2.5	10.5	3.5	8

As judged by the first observations the thermal behaviour of (10a)/(10b) and (14a)/(14b) differs typically: the trans-compounds are stable in solution (C_2Cl_4) up to at least 230°C; at 400°C (vapour phase) 10) (10a) is mainly fragmented into (11a) and ketene. In contrast, (14a) at 140°C (C_2Cl_4, $t_{1/2}$ = 17 min) cleanly isomerises into the cyclonona-2,4,7-trienone (16a), for which the all-cis geometry - in agreement with a [σ2s+σ2s+σ2s]-cycloreversion - is confirmed by the ^{1}H-nmr-spectrum (360 MHz, $CDCl_3$:δ = 6.59 ppm (3-H), 6.40 (2-H), 6.23 (4-H), 6.08 (8-H), 5.78 (7-H), 5.71 (5-H), 3.31 (9-H), 2.75 (6-H); $J_{2,3}$ = 12.5, $J_{3,4}$ = 4.5, $J_{4,5}$ = 11.0, $J_{5,6}$ = 8.5, $J_{6,7}$ = 6.5, $J_{7,8}$ = 10.0, $J_{8,9}$ = 7, $J_{6,8}$ = 1.0, $J_{7,9}$ = 1.0 Hz). (14b) is recovered unchanged up to ca. 220°C. Compared with the still unknown cis-bis-[1.1]-σ-homobenzene (cis-(1); X=Y =CH_2; E_a estimated as 23 ± 2 kcal/Mol 11)) the expected drastic increase in E_a is clearly indicated. From the systematic kinetic study with the ketones (10a)/(10b) and (14a)/(14b), as well as with the corresponding basic skeletons (3) and (4), more insight into the intervention, type and energetic stabilisation of homobenzenoid transition states - e.g. (15a)/(15b) (the H/H-interaction in (14b) becomes even more severe in the early stages of the [2s+2s+2s]-mode of cycloreversion) - is expected.



(a), X = CH_2
(b), X = C_2H_4
(c), X = CH_2CO
(d), X = C_2H_2

With (10a)/(10b) and (14a)/(14b) available their application in the synthesis of the tris-σ-homobenzene-systems (5)-(7) 12) is being investigated. The compounds (17)-(21) are first cis-,α,α,β- and α,β,β-derivatives of (5).



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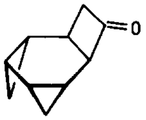

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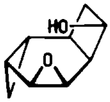

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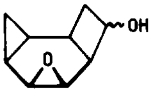

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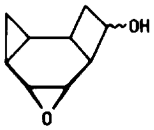

(21)

The new compounds were characterised by elemental analysis, ms-, ir-, ^{1}H- and ^{13}C-nmr data. The cis/trans-relationships in (10a)/(14a) and (10b)/(14b) are clearly established by the coupling constants around the six-membered ring (e.g. table); some marked differences (δ, J) between (14a)/(14b) manifest the distortions in (14b) caused by the very severe H/H-interaction.

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1) Photochemical transformations, part 59.- part 58: H. Prinzbach, K.-H. Lehr, H. Babsch, H. Fritz, Tetrahedron Lett. 1977, 4199.

2) H. Prinzbach, "Homobenzenoid Transition States in $\sigma \longrightarrow \pi$-Isomerisation Reactions", ISNA III, San Francisco, 1977, cit. lit.

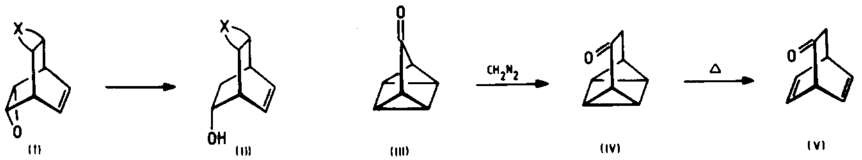
3) Within the σ/π-homobenzene nomenclature the length of the σ-bridges is defined by the number of components given in brackets in decreasing order. The relative orientation of the bridges in the trans-tris-σ-homobenzenes is indicated by α and β, where the side with the longest bridge or - two bridges being equal - with two bridges is the α-side.

4) W.L. Jorgensen, J. Am. Chem. Soc. 97, 3082 (1975); 98, 6784 (1976); P.M. Warner in "Topics in Nonbenzenoid Aromatic Chemistry", Vol. II, Hirokawa Publ. Co.,p. 284, Tokyo,1977; P. Bruckmann, M. Klessinger, Chem. Ber. 111, 944 (1978); cit. lit.

5) I.M. Takakis, W.C. Agosta, Tetrahedron Lett. 1978, 531.

6) K.N. Houk, Chem. Rev. 76, 1 (1976); K. Schaffner, Tetrahedron 32, 641 (1976).

7) Synthesised by reduction (Na/NH_3) of the epoxides (i) and oxidation (CH_2Cl_2, pyridinium chlorochromate, 20°C) of the alcohols (ii). The alternative route to (12a) via (iii)(CH_2N_2,-20°C; besides (iv) the spiroepoxide (R.W. Hoffmann, R. Schüttler, Chem. Ber. 108, 844 (1975)) is formed), (iv) ($t_{1/2}$(CCl_4, 35°C) = 106 min; ^{1}H-nmr (270 MHz, $CDCl_3$):δ = 2.64 ppm (4-H, d, J=3.2 Hz), 2.12 (1(8)-H, m), 1.67 (6(7)-H, m, $J_{1,6}+J_{6,7}$ = 4.5, $J_{2,6}$ = 6 Hz), 1.08 (2(5)-H, m)) and (v)



(^{1}H-nmr (CCl_4):δ=6.2-6.6 ppm (4H, m), 3.65-4.0 (2H, m), 1.68 (2H, d, J=4 Hz) is less advantageous: cyclopropanation of (v) gives preferably (8a) (H.-P. Schal, part of dissertation, Univ. Freiburg).

8) The efforts towards the synthesis of (10c)/(10d) and (14c)/(14d) as well as of (13a)/(13b) by photodecarbonylation of (14a)/(14b) will be reported separately (H. Prinzbach, H.-P. Schal, R. Keller, in preparation).

9) For photo-[$2\pi+2\sigma$]-cycloadditions in analogous systems see H. Prinzbach, H. Fritz, H. Hagemann, D. Hunkler, S. Kagabu, G. Philippossian, Chem. Ber. 107, 1971 (1974).

10) We thank Dr. G. McMullen for the vapour phase experiments.

11) H. Prinzbach, D. Stusche, J. Markert, H.-H. Limbach, Chem. Ber. 109, 3505 (1976).

12) As an approach to (7) or derivatives thereof, [4+2]-additions of cyclobutene-dienophiles to bis-1,1'-cyclobutenyl are being undertaken (D. Burger, part of dissertation, Univ. Freiburg).