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REDUCTIVE TRANSFORMATIONS

2. CIS- AND TRANS-1,2-ADDITION OF ELECTROPHILES TO DIANIONIC π-SYSTEMS [1]

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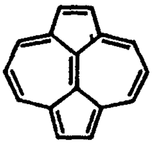
Abstract The dianion salt of a polycyclic π-system is selectively alkylated to yield [14]annulenes with trans- or cis-configuration of the bridging group The products are suitable models for spectroscopic and structural considerations

We have recently described the addition of electrophiles to the dianion salt 2 [1,2] which proceeds via specific attack at the carbons of the inner ethylene bridge This reaction is unique in that it implies the direct transformation of an easily accessible polycyclic (isopyrene) π-system [3,4] into a bridged π-perimeter



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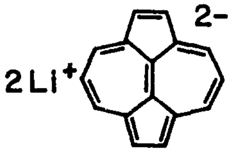

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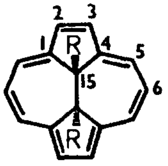

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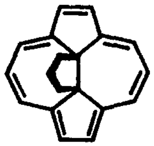
3a R= $-CH_3$
3b R= $-(CH_2)_3Cl$
3c R= $-(CH_2)_8Br$



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It is an attractive feature of the above procedure that it allows for the ready construction of different annulenes As can be inferred from model considerations,only a trans- (not a cis-) configuration of the bridging group leads to a more or less planar conformation of the peripheral π-system. The present work is devoted to realize both alternatives and to compare the resulting π-structures.

In a typical experiment 0.02 molar solutions of dicyclopenta[ef,kl]heptalene (1) in dry, degassed tetrahydrofuran (THF) are reduced with lithium at ca. –20 °C to yield the green-brown solution of 2 which is identified by its NMR-spectra[5] and which can be stored for months. In ammonia, however, the dianion suffers from ready protonation which process can be utilized for the preparation of dihydro- and hydro-alkyl derivatives. Dialkylation of 2 is, thus, only feasible under strictly aprotic conditions.

Quenching of 2 with monofunctional alkylating agents produces only the trans-bisalkyl adduct of the general formula 3[1]. Application of bifunctional electrophiles, e.g. 1,3-dichloropropane (4) affords the desired cis-bridged annulene cis-15,16-propano-1,4:8,11-ethanediylidene[14]annulene (5) (deep red needles, m.p. 124-5 °C). Thereby, the trans-15,16-bis(3-chloropropyl)-1,4:8,11-ethanediylidene[14]annulene (3b) is obtained as side product (red plates, m.p. 194-6 °C). Slow addition of a dilute solution of 4 in dry, degassed THF to the dianion solution (prepared from 100 mg of 1) causes the colour to change from green-brown to red-brown. After work-up and chromatography (aluminium oxide, n-hexane) one obtains 5 (52 mg, 43 %), 3b (6 mg, 3 %) and 1 (1 mg, 1 %). As anticipated, inverse quenching (i.e. the addition of the dianion solution to a large excess of 4 in THF) increases the relative amount of product 3b, the molar ratio of 5, 3b and 1 being 5:3:2.[6]

Two further examples may be mentioned to outline the scope and limitations of the present alkylation procedure. Introducing methylene chloride as the quenching agent does not provide cis-15,16-methano-1,4:8,11-ethanediylidene[14]annulene but leads to a quantitative reoxidation of 2. Furthermore, no ring closure is obtained with long-chain 1,n-dihaloalkanes (e.g. 1,8-dibromooctane). One generates the trans-15,16-bis(8-bromooctyl)-1,4:8,11-ethanediylidene[14]annulene (3c) in 16 % yield (green plates, m.p. 73-4 °C).

The facile preparation of differently bridged annulenes by slight modification of the addition step calls for a comparison of the spectroscopic data (see Table 1). From the obvious deshielding of (outer) ring protons and the shielding of (inner) bridge protons compounds 5, 3a, 3b and 3c are characterized as essentially diatropic. Particularly revealing is the large range of ^{1}H-chemical shifts covered by the resonances of the methylene protons (15a - 15h) within 3c. This sequence nicely visualizes the secondary magnetic field due to the peripheral ring current effect.[8]

When comparing the ^{1}H-NMR-chemical shifts of 5 and 3a the outer (inner) protons of the former exhibit a pronounced shielding (deshielding) so that the effect of the diamagnetic ring current appears smaller in 5 (see below).[9] The electron absorption spectra of 5 and 3b in a qualitative fashion are quite similar [5: λ_{max}(n-hexane)=330 (ϵ=121580), 337 (92370), 390 (7520), 478 (45), 488 (53), 530 (86), 550 (111), 562 (113), 3b: 336 (121479), 350 (87931), 381 (3429), 400 (3695), 425 (4877), 443 (5232), 449 (5689), 504 (59), 512 (74), 556 (130), 583 (148), 611 (551)].[9] It is characteristic, however, that the bands of 5 suffer from a hypsochromic shift.[10] That 5 and 3a are structurally different, although possessing the same configuration of the π-perimeter, is also clear from their ^{13}C-chemical shifts.

Table 1 ^{1}H-(δ_H) and ^{13}C-(δ_C) NMR-chemical shifts ($CDCl_3$) of 5, 3a, 3b, and 3c

		2	5	6	15a	15b	15c	15d	15e	15f	15g	15h
δ_H	5	7.99	8.52	7.94	-0.90	-0.90						
	3a	8.74	8.77	8.04	-4.53							
	3b	8.83	8.78	8.05	-4.57	-1.34	1.84					
	3c$^{a)}$	8.92	8.79	8.13	-4.76	-1.89	-0.45	0.24	0.64	1.04	1.64	3.18

		1	2	5	6	15	15a	15b
δ_C	5$^{b)}$	157.6	129.6	118.9	122.2	58.3	54.4	20.9
			(164)$^{c)}$	(154)	(156)			
	3a$^{b)}$	152.2	134.9	118.9	118.8	42.7	14.7[7]	
			(164)	(153)	(155)			

a) CCl_4 as solvent; b) measured at 20 MHz; c) the data given in parentheses are the corresponding $^{1}J_{CH}$-coupling constants [Hz]

We have recently achieved X-ray analysis of both 5 [12] and 3a [1]. While the detailed results of this work are given elsewhere [13], Figure 1 presents a side view of both structures. The perimeter of 3a can be considered as essentially planar since the ring carbons deviate from the mean plane by not more than

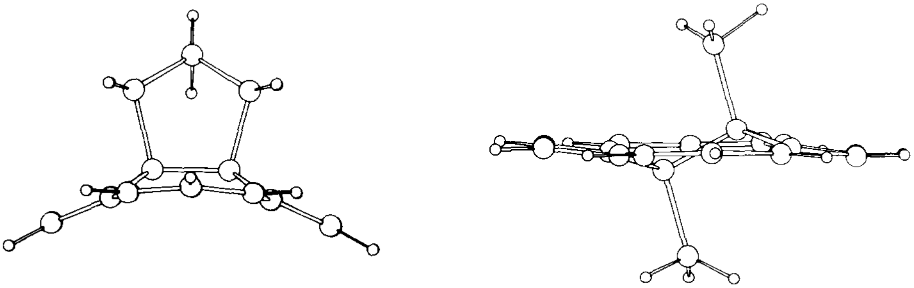
5 **3a**

Figure 1 Side view of 5 and 3a

Δd_{max} = 0.08 Å and the torsion angles τ are between 0.1° and 10.4°. The corresponding parameters for the cis-analogue 5 (Δd_{max} = 0.44 Å, τ between 0° and 20 3°) indicate a bent perimeter The decreasing π,π -overlap in 5 is expected to increase the π-bond fixation. We therefore conclude that, in accordance with related experience [11], the different spectroscopic data of 5 and 3 reflect the change of the ring conformation

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References and Notes

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6 The use of highly concentrated THF-solutions of 4 favors the formation of 1, not of 3b. One concludes that reductive cleavage of the quenching agent effectively competes with the S_N-process One cannot rigorously exclude that there occurs some electron transfer process prior to C-C-bond formation; see R D. Guthrie in "Comprehensive Carbanion Chemistry", Part A, (E. Buncel, T. Durst, eds), ch. 5, Elsevier, 1980

7 The assignment of (proton-bearing) carbons of the 5- and 7-membered rings follows from the $^1J_{CH}$-coupling constants Note that in comparison with ref 1 the ^{13}C-signals of 3a have to be reassigned

8 V Boekelheide, Pure Appl Chem 44 (1975) 751, and references cited therein

9 Clearly, the different geometries of 3a and 5 (orientation of the CH-bonds, projected ring area) do not allow a direct comparison of the δ_H-data in terms of "ring current intensities".

10 Additional physical data of 5: m/e 244 (37 %, M^+), 229 (12 %, $M^+ - CH_3$), 215 (100 %, $M^+ - C_2H_5$), 202 (83 %, $M^+ - C_3H_6$) 5 gives a satisfactory combustion analysis.

11 E. Vogel, Isr. J. Chem. 20 (1980) 215; and references cited therein.

12 5 crystallizes in the tetragonal space group P4_2mc with a = 10 568(2) and c = 5 899(3) Å, Z=2, $\rho_{ber.}$ = 1.232 g/cm^3 The intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Mo K_α radiation 283 reflections were used in the structure determination The structure was solved by direct methods, all hydrogens were located in difference maps. Anisotropic refinement of the non-hydrogen atoms by least squares yielded a final R value of 0 056. The electron density distribution resulting from the E maps of both 5 and 3a indicates the superposition of two annulene molecules.

13 J Lex, to be published

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