CHIMIA 41 (1987) Nr. 12 (Dezember)

Synthesis and Photochemistry of Tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene Based Systems**

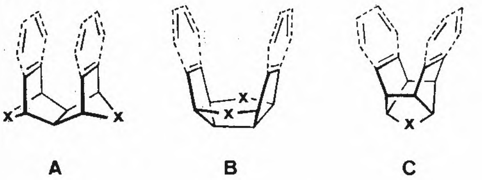
Johann P. Melder, Fabian Wahl, Hans Fritz, and Horst Prinzbach*

Abstract: $C_{14}H_{14}$ tetracyclic tetraene **1** and its benzoanellated derivatives **2, 3** are sought as versatile intermediates. Preparatively useful syntheses have been worked out for the key intermediates (diketones **10–12**). From **10, 11** the compounds **1, 2** are obtained. These unsaturated hydrocarbons undergo regioselectively [2 + 2]- (quantitative) and [6 + 2]- (2:1 equilibrium) cycloaddition, respectively, upon excitation with monochromatic λ = 254 nm light.

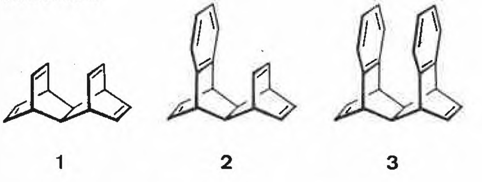
A prominent goal in our studies with bichromophoric substrates **A–C** (Scheme 1) is the elucidation of the structural/stereoelectronic prerequisites for the photochemical formation of benzo/benzo [6 + 6]-cycloadducts. The latter are sought inter alia as intermediates on the way to structurally modified pagodanes[1] and isopagodanes[2,3], unusual dications[4], and novel polycycles (e.g. modified dodecahedranes)[5]. The intricacies of this relationship between structure and photoreactivity are underlined by the fact that [6 + 6]-cycloadducts can be produced in diverse dibenzo **A**- (X = CH_2, CHOR, C_6H_4), but not in dibenzo **B/C**-systems, in spite of seemingly rather similar structural situations[6]. Especially perplexing is the recent finding by *Grimme* et al.[7] that no adduct formation takes place after homologation of dibenzo **A** with X = CH_2 to X = $(CH_2)_2$[8]. A potential cause – greater flexibility of the molecular skeleton and, therefore, efficient vibrational desactivation of the excited states – should be eliminated in the more rigid dibenzodiene **3** derived from the $C_{14}H_{14}$ tetraene **1** (tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene) and its (2α, 3β, 6β, 7α)-4,5-benzo derivative **2** (Scheme 2). Preliminary preparative and photochemical results in the series **1–3** are presented in this communication.

In Schemes 3 and 4, the synthesis of the diketones **10–12** and of the target substrates **1, 2** is delineated[11]. The isodrin-analogue **4**, the common starting material for **10–12**, was prepared as described by *Wege* et al.[12] from *tert*-butoxynorbornadiene and tetrachlorocyclopentadienone dimethyl acetal in 40% yield, after separation from isomeric adducts. Transformation of **4** via ketoalcohol **7** (*m.p.* 93 °C) to the diketone **10** (tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene-11,12-dione), using conventional methodology, was straightforward (overall 65–70%; colourless crystals, *m.p.* 121 °C (dec.), $\nu_{C=O}$ = 1770 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ = 5.83 (t, 4-, 5-, 9-, 10-H), 3.25 (t, 1-, 3-, 6-, 8-H), 3.00 (m, 2-, 7-H))[13]. Again, the route to the 4,5-benzodiketone **11** via regiospecific anellation of **4** on the sterically less hindered C4=C5 double bond with tetrachlorothiophenedioxide followed by rapid dyotropic hydrogen migration to give **5** (*m.p.* 277 °C) and via ketoalcohol **8** (*m.p.* 109 °C (dec.)) proceeded smoothly (overall 55–60%, colourless crystals, *m.p.* 133 °C (dec.); $\nu_{C=O}$ = 1760, 1750 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ = 7.24 (m, 2 H), 7.10 (m, 2 H), 5.17 (m, 9-, 10-H), 3.64 (m, 3-, 6-H), 3.08 (m, 1-, 2-, 7-, 8-H)). With respect to the 4,5:9,10-dibenzodiketone **12**, the dibenzodimethylether **9** had already been approached[15]

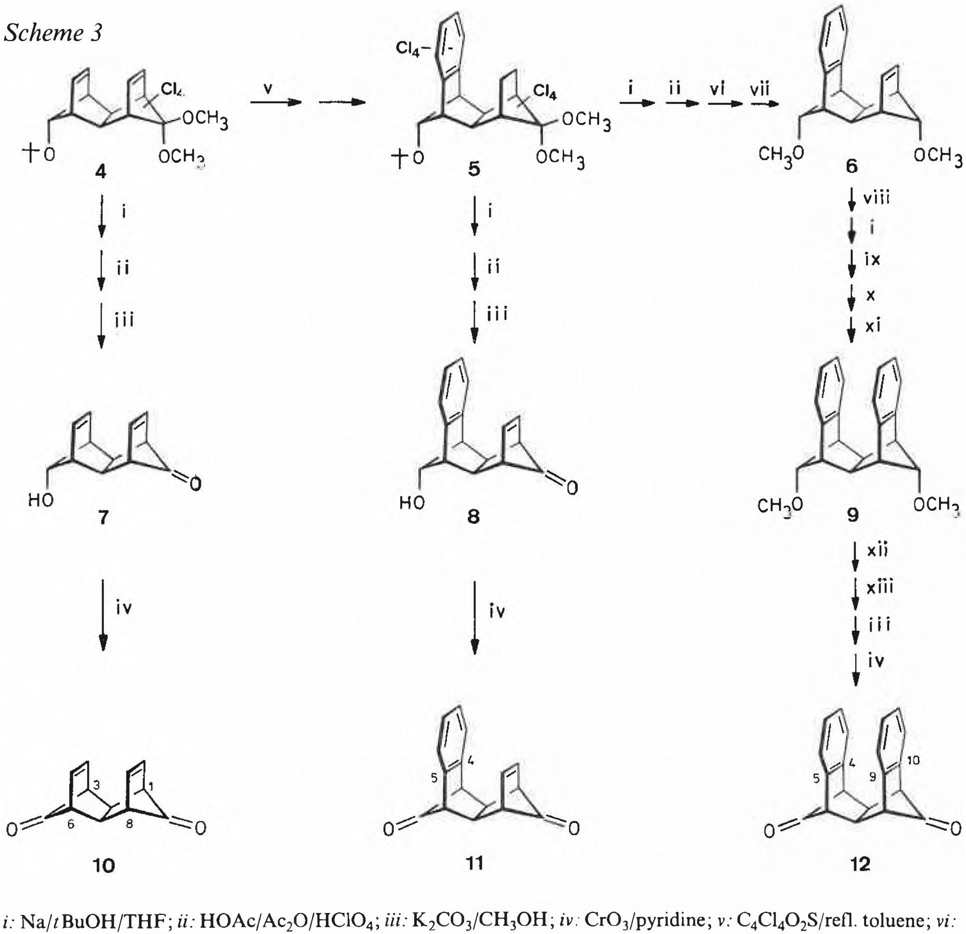
Scheme 1



Scheme 2



Scheme 3



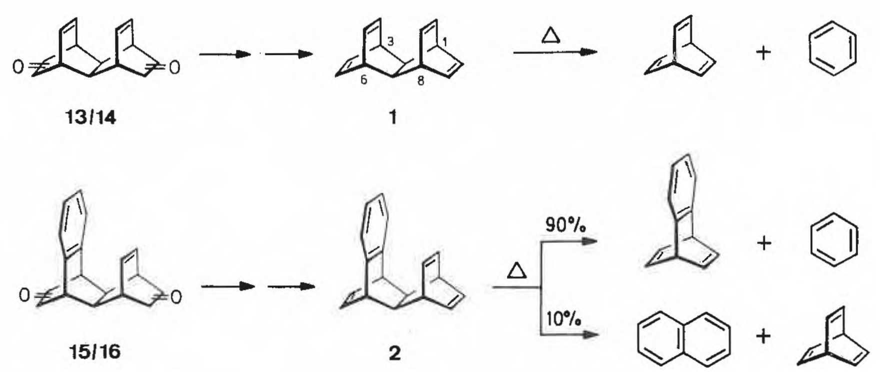
i: Na/*t*BuOH/THF; *ii:* HOAc/Ac_2O/$HClO_4$; *iii:* K_2CO_3/CH_3OH; *iv:* CrO_3/pyridine; *v:* $C_4Cl_4O_2S$/refl. toluene; *vi:* Li[HAl(O*t*Bu)$_3$]/THF; *vii:* NaH/CH_3I; *viii:* $C_5Cl_4(OCH_3)_2$/refl. xylene; *ix:* H_2SO_4 (30%)/CH_2Cl_2; *x:* refl. CCl_4; *xi:* Pd/C, 190 °C, 60 min; *xii:* $(CH_3)_3SiI/CHCl_3$, room temperature; *xiii:* AgOAc/refl. HOAc.

---

* *Correspondence:* Prof. Dr. H. Prinzbach
Institut für Organische Chemie und Biochemie
Chemisches Laboratorium der Universität
Albertstrasse 21, D-7800 Freiburg i.Br.
(Bundesrepublik Deutschland)

** Photochemical Transformations, Part 73. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG. – Part 72: W. Marterer, H. Fritz, H. Prinzbach, *Tetrahedron Lett. 28* (1987) 5497.

Scheme 4



13/14

1

15/16

2

as an intermediate en route to pagodanetetrone or functionalized dodecahedranes[1,5]. The annelations of **4** to give **6** (*m.p.* 71 °C) and of **6** to give **9** (*m.p.* 161 °C) were achieved through four- and five-step reaction sequences with overall yields of 65–70 and 35–40%, respectively. In the second benzoanellation, the drastic conditions for the final dehydrogenation were once more[1] responsible for the substantial material loss (ca. 50%). Cleavage of the C-11(12)–O bonds in **9** by $(CH_3)_3SiI$[16] (with complete retention at C-11(12)) necessitated the rather lengthy procedure (overall 58–62%) for the transformation to **12** (colourless crystals, *m.p.* 246 °C (dec.)). For **12** the UV/NMR spectra reveal the expected consequences[1] of two proximal face-to-face oriented benzene rings ($\nu_{C-O} = 1760\ cm^{-1}$; UV($CH_3CN$): λ_{max} (ε) = 302 (860), 270 (2270), 262 (1930), 244 (3220), 225 nm (5010); ^1H-NMR ($CDCl_3$): δ = 6.80 (s, 8H), 3.72 (t, 1-, 3-, 6-, 8-H), 3.26 (m, 2-, 7-H); ^{13}C-NMR ($CDCl_3$): δ = 194.2 (C-11, -12), 133.9 (C-4, -5, -9, -10), 127.9 (C-15, -16, -19, -20), 124.4 (C-13, -14, -17, -18), 52.0 (C-1, -3, -6, -8), 32.7 (C-2, -7)).

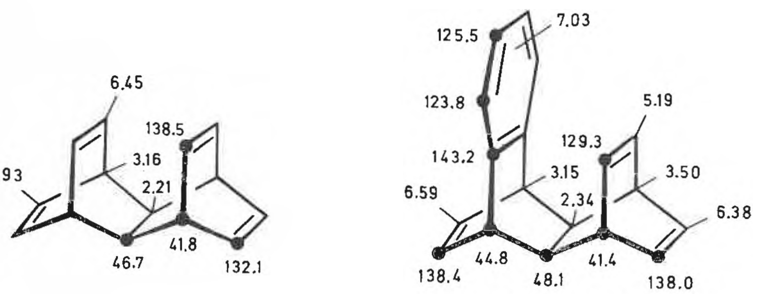
Ring enlargement of **10** and **11** (not yet of **12**) was performed with diazoacetic ester/BF_3, as CH_2N_2/LiCl furnished mainly epoxides. After saponification and decarboxylation (under pressure) of the corresponding ketoesters (50–60%, not optimized), the resulting mixtures of diastereomeric diketones **13/14** and **15/16** were subjected to Bamford-Stevens olefination (35–40%)[17].

The hydrocarbons **1** ($C_{14}H_{14}$) and **2** ($C_{18}H_{16}$), both isolated as colourless crystals (*m.p.* 67 °C and 74 °C, respectively), on heating to 160 °C (degassed perchlorobutadiene solutions) undergo [4 + 2]-cycloreversions ($t_{1/2}$ ca. 60 min): **1** cleanly to benzene/barrelene, **2** to benzene/benzobarrelene (ca. 90%) and naphthalene/barrelene (ca. 10%) – in agreement with the MS-fragmentation patterns. The UV as well as ^1H- and ^{13}C-NMR data (Scheme 5) are indicative of the proximity of the C4=C5/C9=C10 chromophors.

Tetraene **1** features a 1,6-(**a**) and two 1,4-homodiene (**b**) chromophors, with calculated (MM2[20]) through-space distances *d* (probably somewhat too short[1,3]) and interorbital angles ω (Scheme 6), which are in good agreement with the data for the model 1,6- and 1,4-dienes **17** (*d* for $X = (CH_2)_n$: 2.87 Å (n = 1), 2.94 Å (n = 2), 3.01 Å (n = 3))[21] and **18** (*d* (ω) for $X = (CH_2)_n$: 2.36 Å (112°) (n = 1), 2.42 Å (117°) (n = 2), 2.45 Å (130°) (n = 3))[22]. In **17** and **18**, photo-[2 + 2]-addition reactions proceed slower for $X = (CH_2)_2$ than for $X = CH_2$ but still selectively[23,24]. In comparison, the photochemical outcome, intercyclic vs. intracyclic [2 + 2]-addition, in 1,7-/1,4-homodiene substrates of type **20** depends critically on the relative *d*/ω values (variation of X)[25].

Direct excitation of **1** (ca. 10^{-2}M, degassed *n*-pentane solutions, room temperature) with monochromatic λ = 254 nm light from a low-pressure Hg lamp causes exclusive and quantitative formation of the known hexacyclic diene **21**[2] (Scheme 7). The presumably rather labile[26] isomers **22/23** have not been observed at −40 °C, what should tend to exclude their fleeting intermediacy. Clearly, the advantage of the shorter distance in **1b** is offset by the almost ideal interorbital angle in **1a**[28]. For benzotriene **2**, under the same conditions at various irradiation times, a ca. 2:1 photoequilibrium with the [6 + 2]-adduct **24** (heptacyclo[$8.7.1.0^{2,7}.0^{2,9}.0^{7,15}.0^{8,13}.0^{14,18}$]-octadeca-3,5,11,16-tetraene) is established. Again no [2 + 2]-/[6 + 2]-addition in the bicyclo[2.2.2]octadiene units was detected. Only to a very minor extent (< 1%) did competition by [4 + 2]-reversion become evident in the formation of naphthalene. By chromatography, **24** was isolated as a crystalline material (^1H-NMR ($CDCl_3$): δ = 6.32 (m, 16-, 17-H), 6.17 (m, 11-, 12-H), 5.57 (m, 3-, 6-H), 5.42 (m, 4-, 5-H), 2.74 (m, 10-, 13-H), 2.51 (m, 8-, 9-H), 2.43 (m, 1-, 15-H), 1.70 (m, 14-, 18-H); ^{13}C-NMR ($CDCl_3$): δ = 132.5 (C-16, -17), 130.5 (C-11, -12), 129.2 (C-4, -5), 122.1 (C-3, -6), 52.9 (C-8, -9), 50.4 (C-2, -7), 45.0 (C-14, -18), 44.5 (C-1, -15), 39.0 (C-10, -13)). The UV absorption curve with λ_{max} = 285 nm (ε = 1300) and long tailing (ε_{310} = 450) explains that **24** was not found after irradiation of **2** (low absorption beyond λ = 285 nm, ε_{285} = 65) in benzene solution with a high-pressure Hg lamp

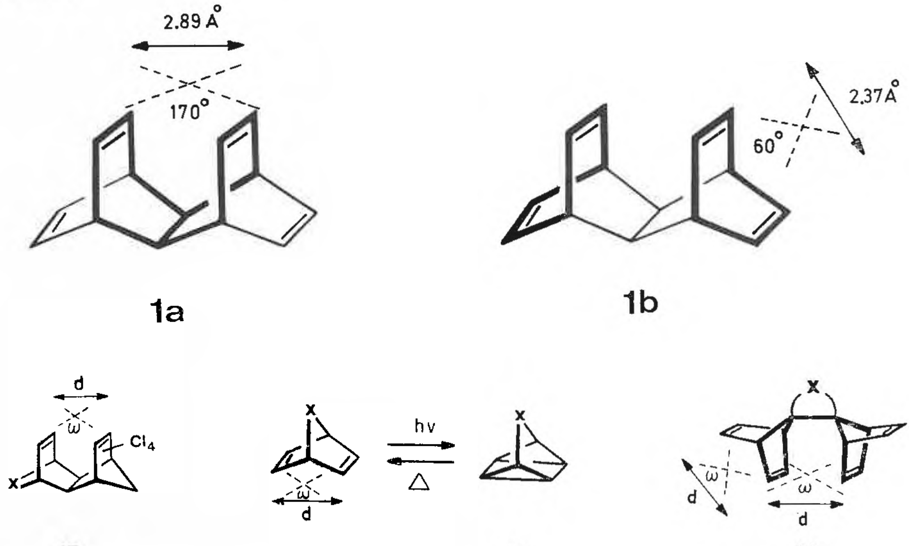
Scheme 5



λ_{max} (ε): 254 nm (210)
(*i*-octane)

276 nm (350), 268 (500), 245 (880)

Scheme 6



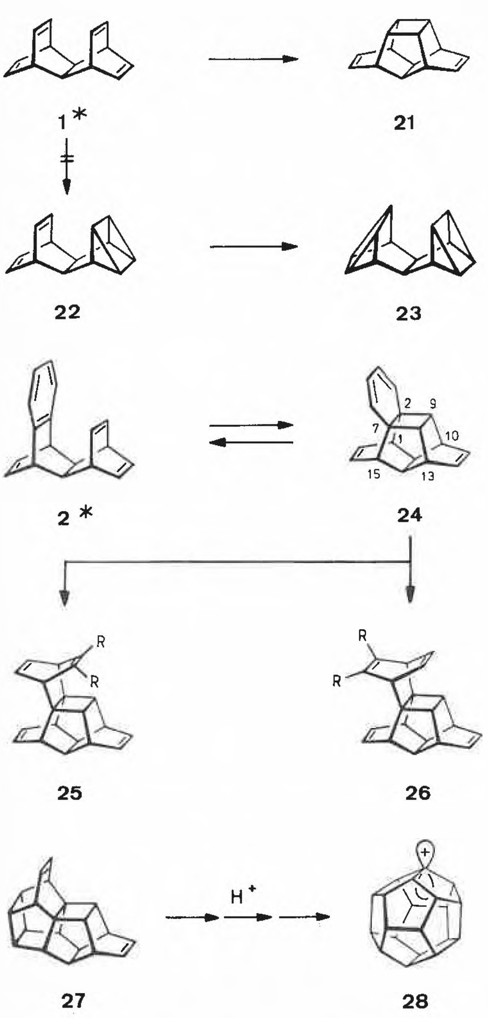
17

18

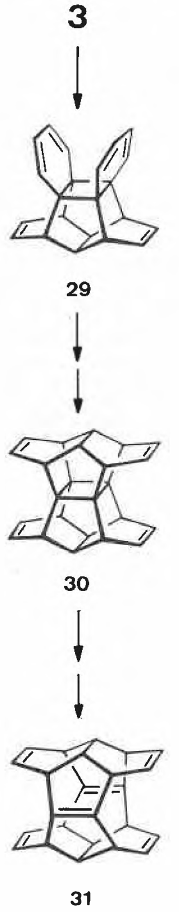
19

20

Scheme 7



Scheme 8



through Pyrex and that **24** is isomerized back to **2** under these conditions (and slowly on standing in daylight). In sensitized irradiation experiments (acetone) with **1** and **2**, as yet not elucidated processes compete with the formation of **21** and **24**, respectively. In solution (perchlorobutadiene), **24** remained unchanged up to at least 180°C; dimethyl acetylenedicarboxylate was added (toluene, 110 °C) to give quantitatively a ca. 9:1 mixture of the *endo-/exo*-adducts **25**/**26**[29]. The corresponding $C_{20}H_{18}$ hydrocarbon (R = H) and its even more strained valence isomer **27** are being investigated as potential precursors of the presumably rather stable $C_{20}H_{19}$ dodecahedryl cation **28**[4,30].

Good chances are seen now that the analogies between **1** and **2** and the respective A-structures with X = CH_2 extend to the dibenzo-analogues and that the [6 + 6]-addition **3**→**29** can be realized. A relatively efficient route would then be open towards chemically versatile target frameworks like [2.2.2.2]pagodatetraene **30** and tetracosahexaene **31** (Scheme 8). The obvious alternative, photo-[6 + 6]-addition at the stage of diketone **12** (or e.g. **9**) followed by ring enlargement/olefination, is complicated by the proclivity of such (thermally very stable[1,31]) *syn-o,o'*-dibenzene structures towards acid-catalyzed cleavage into the dibenzo-isomers.

Received: September 25, 1987 [FC 119]

---

[1] W.-D. Fessner, G. Sedelmeier, P.R. Spurr, G. Rihs, H. Prinzbach, *J. Am. Chem. Soc. 109* (1987) 4626.

[2] G. Sedelmeier, W.-D. Fessner, R. Pinkos, C. Grund, Bulusu A. R. C. Murty, D. Hunkler, G. Rihs, H. Fritz, C. Krüger, H. Prinzbach, *Chem. Ber. 119* (1986) 3442.

[3] Bulusu A. R. C. Murty, P. R. Spurr, R. Pinkos, C. Grund, W.-D. Fessner, D. Hunkler, H. Fritz, W. R. Roth, H. Prinzbach, *Chimia 41* (1987) 32.

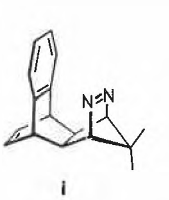
[4] G. K. S. Prakash, V. V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G. A. Olah, W.-D. Fessner, H. Prinzbach, *J. Am. Chem. Soc. 108* (1986) 836; H. Prinzbach, Bulusu A. R. C. Murty, W.-D. Fessner, J. Mortensen, J. Heinze, G. Gescheidt, F. Gerson, *Angew. Chem. Int. Ed. Engl. 26* (1987) 457.

[5] W.-D. Fessner, Bulusu A. R. C. Murty, H. Prinzbach, *Angew. Chem. Int. Ed. Engl. 26* (1987) 451; W.-D. Fessner, Bulusu A. R. C. Murty, J. Wörth, D. Hunkler, H. Fritz, H. Prinzbach, W. D. Roth, P. v. R. Schleyer, A. B. McEwen, W. F. Maier, *ibid. 26* (1987) 452; P. R. Spurr, Bulusu A. R. C. Murty, W.-D. Fessner, H. Fritz, H. Prinzbach, *ibid. 26* (1987) 455; H. Prinzbach, W.-D. Fessner, *J. Appl. Chem.*, in press.

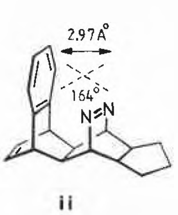
[6] G. Sedelmeier, W.-D. Fessner, C. Grund, P. R. Spurr, H. Fritz, H. Prinzbach, *Tetrahedron Lett. 27* (1986) 1277; W.-D. Fessner, G. Sedelmeier, L. Knothe, H. Prinzbach, G. Rihs, Z.-Z. Yang, B. Kovac, E. Heilbronner, *Helv. Chim. Acta 70* (1987) 1816.

[7] W. Grimme, personal communication.

[8] A similar discrepancy exists for benzo/azo compounds: **i**[9], not, however, **ii**[10], undergoes [6 + 2]-photocycloaddition.



i



ii

[9] K. Beck, S. Hünig, *Angew. Chem. Int. Ed. Engl. 25* (1986) 187.

[10] G. Fischer, E. Beckmann, H. Prinzbach, G. Rihs, J. Wirz, *Tetrahedron Lett. 27* (1986) 1273.

[11] All new compounds are fully characterized by elemental analysis and spectral data (IR, UV, ^{1}H- and ^{13}C-NMR).

[12] L. T. Byrne, A. R. Rye, D. Wege, *Aust. J. Chem. 27* (1974) 1961; cf. K. B. Astin, K. J. McKenzie, *J. Chem. Soc. Perkin Trans. I* (1975) 1004; G. Mehta, M. S. Nair, *J. Am. Chem. Soc. 107* (1985) 7519.

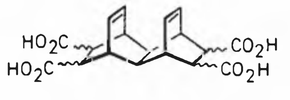
[13] A similar though more laborious route to **10** is described in the dissertation of B. Albert, Universität Düsseldorf (1981) (we thank Prof. H.-D. Martin for a copy); discrepancies with respect to the precursors (e.g. the intermediate taken there for **7** is actually the 11-epimer) are caused by the false assignment of starting material in the original reference[14] (in ref.[2] compound **2** has to be reassigned as **3**, **3** as **4**, and **4** as **2**).

[14] G. Sedelmeier, dissertation, Universität Freiburg i. Br. (1979).

[15] Part of the forthcoming dissertation of J. P. Melder, Universität Freiburg i. Br.

[16] M. E. Jung, M. A. Lyster, *J. Org. Chem. 42* (1977) 3761.

[17] Oxidative degradation (i.a. $Pb(OAc)_4$, $Ni(CO)_2(PPh_3)_2$[18]) of the known tetraacid **iii**[19] has given rise to only traces of tetraene **1**.



iii

[18] B. M. Trost, F. Chen, *Tetrahedron Lett. 12* (1971) 2603.

[19] E. LeGoff, S. Oka, *J. Am. Chem. Soc. 91* (1969) 5665.

[20] N. L. Allinger, *J. Am. Chem. Soc. 99* (1977) 8127.

[21] D. C. Dong, W. Wong-Ng, S. C. Nyburg, P. Y. Siew, J. T. Edward, *Can. J. Chem. 62* (1984) 452.

[22] E. Heilbronner, *Isr. J. Chem. 10* (1972) 143; H. Prinzbach, H.-G. Schmidt, *Chem. Ber. 107* (1974) 1988.

[23] D. C. Dong, J. T. Edward, *J. Org. Chem. 45* (1980) 2395.

[24] H. Prinzbach, *Pure Appl. Chem. 16* (1968) 17; H. Prinzbach, W. Eberbach, G. Philippossian, *Angew. Chem. Int. Ed. Engl. 9* (1970) 887; H. Prinzbach, W. Eberbach, H. Hagemann, G. Philippossian, *Chem. Ber. 107* (1974) 1957; H. Prinzbach, H. Fritz, H. Hagemann, D. Hunkler, S. Kagabu, G. Philippossian, *ibid. 107* (1974) 1971; R. S. H. Liu, *Tetrahedron Lett. 10* (1969) 1409; S. F. Nelsen, J. P. Gillespie, *ibid. 10* (1969) 3259, 5059.

[25] H. Prinzbach, K. Weidmann, S. Trah, L. Knothe, *Tetrahedron Lett. 22* (1981) 2541; S. Trah, K. Weidmann, H. Fritz, H. Prinzbach, *ibid. 28* (1987) 4399.

[26] The kinetic barrier for the $2\sigma \rightarrow 2\pi$ isomerization in the tetracycles **19** is much lower when X is a (saturated) two- rather than a one-carbon bridge (ΔE_a=10–12 kcal/mol; $t_{1/2}$ (35°C) for **19** with X = CH_2CO amounts to 106 min)[23,27].

[27] H. Prinzbach, H.-P. Schal, D. Hunkler, *Tetrahedron Lett. 19* (1978) 2195; S. Kagabu, dissertation, Universität Freiburg i. Br. (1975); H.-P. Schal, dissertation, Universität Freiburg i. Br. (1980).

[28] Such a regiospecificity of photocycloaddition (sun light, sun lamp) was recently reported for an additionally bridged tetraene of type **1** (*d* = 2.98Å, X-ray) which had resulted (11% yield) from high-pressure addition of dicyanoacetylene to 11-methylene-1,6-methano[10]annulene: F.-G. Klärner, B. M. J. Dogan, R. Weider, D. Ginsburg, E. Vogel, *Angew. Chem. Int. Ed. Engl. 25* (1986) 346.

[29] We are grateful to Dipl.-Chem. R. Pinkos for his assistance.

[30] P. E. Eaton, *Tetrahedron 35* (1979) 2189, and cit. lit.

[31] W. v. E. Doering, W. R. Roth, R. Breuckmann, J.-J. Figge, L. Figge, H.-W. Lennartz, W.-D. Fessner, H. Prinzbach, *Chem. Ber.*, in press.