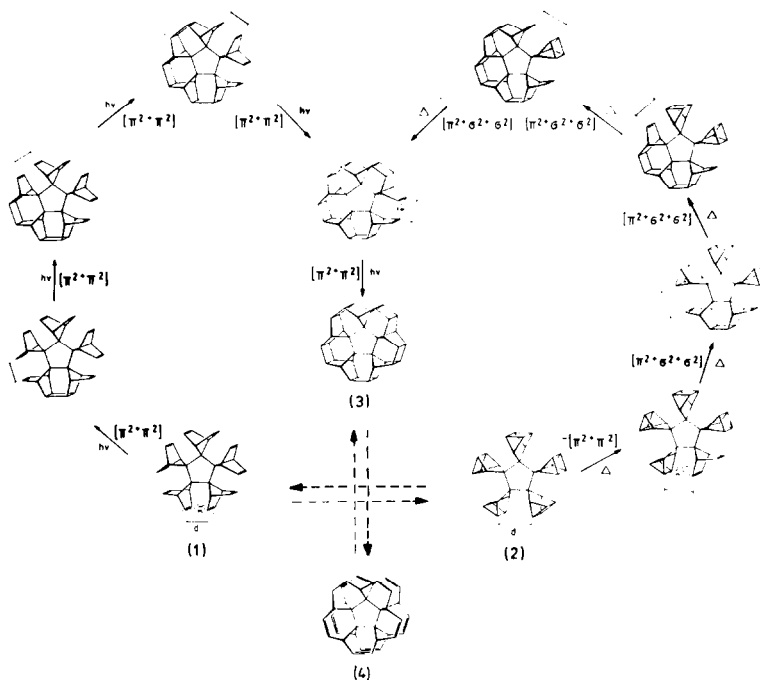


INTERCYCLIC $[\pi_2+\sigma_2+\sigma_2]$ - AND $[\pi_2+\pi_2]$ -CYCLOADDITION REACTIONS
 IN STERICALLY FIXED NORBORNADIENE-/QUADRICYCLANE-SYSTEMS

Horst Prinzbach*, Klaus Weidmann, Stephan Trah and Lothar Knothe
 Chemisches Laboratorium der Universität Freiburg i.Br., BRD

The stereoelectronic prerequisites for unusual "zipper-type" $[\pi_2+\sigma_2+\sigma_2]$ - and $[\pi_2+\pi_2]$ -reaction sequences, e.g. in the still unknown C_7H_6 -pentamers (1)/(2), are being studied using model compounds with systematically varied geometrical parameters. In line with expectations based on model considerations, in the [3]-series ((6),(7)) intracyclic, in the [5]-series ((10),(11)) intercyclic processes clearly predominate.

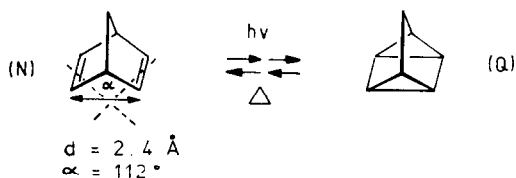
In connection with the question of co-operativity in the formation (scission) of more than two carbon-carbon-bonds ¹⁾ the interconversion of the $C_{35}H_{30}$ -isomers (1)-(4) is of interest. Mechanistically as well as preparatively attractive routes to the heneicosacyclic hydrocarbon



Scheme 1

(3) are the sequences of photochemical and thermal $[\pi_2+\pi_2]$ - and $[\pi_2+\sigma_2+\sigma_2]$ -cycloaddition reactions in the pentanorbornadienylidene (1) and the pentaquadricyclanylidene (2) formulated in Scheme 1. Similar goals are also being pursued with the analogous C_7H_6 -trimers, -tetramers and -hexamers ²⁾. With the route (1) \rightarrow (3) it is presupposed, that the intercyclic $[\pi_2+\pi_2]$ -

photocycloadditions - irrespective of the order of the five single steps - are faster than the intracyclic norbornadiene \rightarrow quadricyclane isomerisations ((N) \rightarrow (Q))³⁾, which would eventually lead to (2). Similarly for the four thermal $[\pi_2+\sigma_2+\sigma_2]$ -steps⁴⁾ in the route (2) \rightarrow (3) a necessary prerequisite is, that the additions of a non-activated but favourably located norbornene-C=C-double bond to a quadricyclane

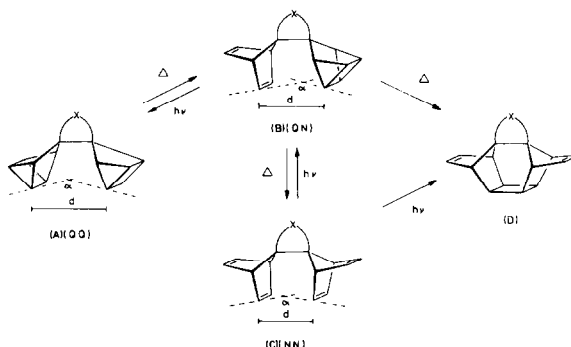


bornene-C=C-double bond to a quadricyclane framework are faster than the quadricyclane \rightarrow norbornadiene isomerisations ((Q) \rightarrow (N), $E_a = 38.3 \text{ kcal/mole}$ ⁵⁾), which would ultimately yield (1).

Inter alia for the experimental substantiation of the assumptions inherent in Scheme 1 model compounds of the types (B)/(C), in which the interorbital distances (d) and interorbital angles (α) are systematically varied by altering the bridge X, are currently being synthesised⁶⁾. From their estimated data it becomes obvious, to what extent an enlargement of X leads to a decrease in the distances and interorbital angles. Clearly, in the [3]-series with its almost ideal orbital orientations the distances are extremely, if not too, large for the interorbital

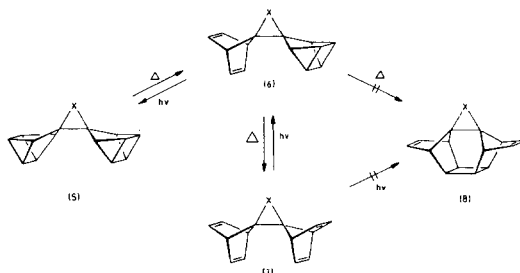
[X+2]	(A)	(B)	(C)
	$d(\text{Å})$ $\alpha(^{\circ})$	$d(\text{Å})$ $\alpha(^{\circ})$	$d(\text{Å})$ $\alpha(^{\circ})$
[3]	4.7 ₀ 180	4.2 ₅ 185	3.7 ₅ 190
[4]	3.6 ₅ 150	3.1 ₅ 155	2.5 ₅ 160
[5]	3.0 ₀ 133	2.4 ₀ 138	1.8 ₅ 142
[6]	2.5 ₀ 120	1.9 ₅ 125	1.3 ₅ 131

(planar)



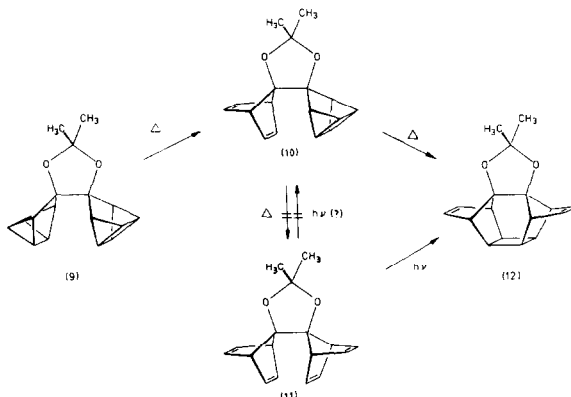
[5]-series, the stereoelectronic situation is undoubtedly favourable for these processes (cf (N) \rightarrow (Q)).

These expectations have been fully confirmed: From known biquadricyclanylidene⁷⁾ the [3]-derivatives (5) (X = CH₂, m.p. 138°C, X = O, m.p. 144°C⁸⁾) have been synthesised. In case of



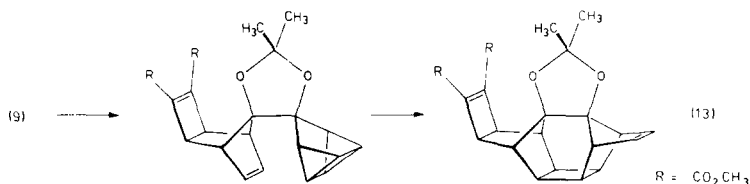
the hydrocarbon (7) the PE-analysis indicates a through-space interaction between the inner C=C double bonds ($\beta = 0.3 \text{ eV}$)⁹⁾. Upon heating (135°C, benzene) the compounds (5) are transformed

via (6) into (7) (e.g. X = CH₂, m.p. 95-96°C), with no indication for any competition from (6) → (8) (¹H-nmr, < 2%). In line with the thermal stabilisation in (6) is the photolysis of (7): Using conditions proven for selective (N) → (Q) isomerisation (acetone sensitisation)³⁾ the products (8) are once again not observed; only the conventional transformation into (6) and (5) is realised. Members of the [4]- (and [6]-) series not yet being available¹⁰⁾ the ketal (9)¹¹⁾ has been studied as a prototype of the [5]-series. Upon heating in benzene solution (135°C) the [_π2+_σ2+_σ2]-adduct (12) (m.p. 121-123°C) is isolated quantitatively. Its thermal stability (up to at least 200°C) is in agreement with the report¹²⁾, that a simple



derivative (monoene) of this framework is a product of the vapour phase pyrolysis (Pt) of Binor-S. The ease of the intermolecular addition (10) → (12), as compared with the homolytic cleavage (9) → (10) (and (10) → (11)), is qualitatively evident from the fact, that already at 75°C the intermediate (10), obtained from (9) at 20°C using PdI₂[Sb(C₆H₅)₃]₂-catalyst, cycloadds to give (12) with a comparable rate (an additional indication is the fact, that the steric fixation provided by the ketal ring is not a conditio sine qua non¹¹⁾). Again the results of the sensitised excitation of the rather labile (strained) tetraene (11) - prepared catalytically from (9) via (10) - complement the thermal behaviour of the diene (10). When (11) is irradiated in acetone solution the intermolecular [_π2+_π2]-cycloaddition clearly predominates. The not-yet-optimised yield of (12) amounts to 70%. The by-product (~15%) is neither (10)/(9) nor an oxetane (acetone addition product).

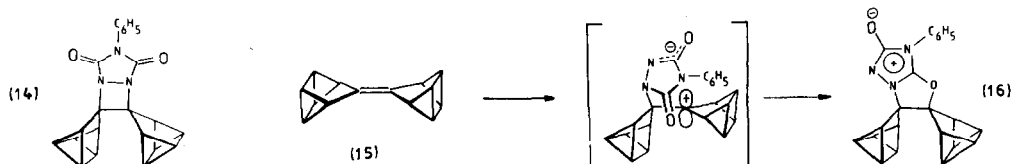
The favourable situation in the [5]-series for intermolecular processes is also manifest in the reactions with bishomodienophilic reagents. From (9) and e.g. an excess of dimethyl



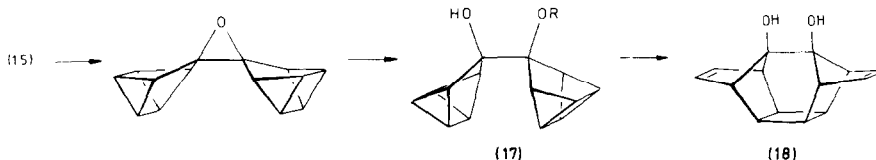
acetylenedicarboxylate predominantly the monoadduct (13) (60-70%, m.p. 173°C) is obtained together with a small amount of the symmetrical 1:2-adduct (<5%).

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

- 1) H. Prinzbach, K.-H. Müller, C. Kaiser, D. Hunkler, *Tetrahedron Lett.* 1980, 3475, cit. lit.
- 2) Cf. the series of [n]-rotanes: L. Fitjer, *Angew. Chem.* 88, 804 (1976); *Angew. Chem. Int. Ed. Engl.* 15, 763 (1976), cit. lit.
- 3) Review: H. Meier in *Houben-Weyl*, Volume 4/5a (Photochemie I), p. 232, Thieme Stuttgart, 1975; G. Kaupp, *ibid.* p. 284; cf. A.J.G. Barwise, A.A. Gorman, R.L. Leyland, P.G. Smith, M.A.J. Rodgers, *J. Am. Chem. Soc.* 100, 1814 (1978), cit. lit.
- 4) C.D. Smith, *J. Am. Chem. Soc.* 88, 4273 (1966); G. Kaupp, H. Prinzbach, *Chem. Ber.* 104, 182 (1971); E. Haselbach, H.-D. Martin, *Helv. Chim. Acta* 57, 472 (1974).
- 5) J.R. Edman, *J. Org. Chem.* 32, 2920 (1967); D.S. Kabakoff, J.-C.G. Bünzli, J.F.M. Oth, W.B. Hammond, J.A. Berson, *J. Am. Chem. Soc.* 97, 1510 (1975).
- 6) K. Weidmann, Thesis, Univ. Freiburg, in preparation.
- 7) H. Sauter, H.-G. Hörster, H. Prinzbach, *Angew. Chem.* 85, 1106 (1973); *Angew. Chem. Int. Ed. Engl.* 12, 991 (1973).
- 8) The new compounds have been fully characterised (elemental analysis, MS, IR, ^1H -, ^{13}C -nmr)
- 9) B. Kovač, E. Heilbronner, H. Prinzbach, K. Weidmann, *Helv. Chim. Acta* 62, 2841 (1979).
- 10) Upon attempting to obtain a modified [4]-derivative (14) from biquadricyclanylidene (15) and N-phenyl-1,2,4-triazolinedione, exclusive addition to the central C=C-double bond takes place to give a crystalline, unstable 1:1-adduct (MS), which according to the ^1H - and ^{13}C - nmr spectra cannot be (14); the triazolium-olate structure (16) is plausible (K.-H. Lehr, J. Werp, H. Bingmann, C. Krüger, H. Prinzbach, *Chem. Ber.*, in press).



- 11) The reaction of (15) with *m*-chloroperbenzoic acid can be directed to yield either the epoxide (5) (X=O) or the mono-*m*-chlorobenzoate (17) (R=*m*-ClC₆H₄CO). Heating (135°C) the diol (17) (R=H) leads uniformly to the [$\pi_2 + \sigma_2 + \sigma_2$]-adduct (18) (m.p. 225-227°C; 80%).



- 12) F.S. Hollowood, M.A. McKervey, R. Hamilton, J.R. Rooney, *J. Org. Chem.* 45, 4954 (1980).

(Received in Germany 7 April 1981)