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CYCLOPROPANATION OF TRICYCLO[5.2.1.0^{4,10}]DECA-2,5,8-TRIENE (TRIQUINACENE)[1]

Dieter Bosse und Armin de Meijere [*]
Organisch-Chemisches Institut der Universität, D-3400 Göttingen
Windausweg 2, Germany

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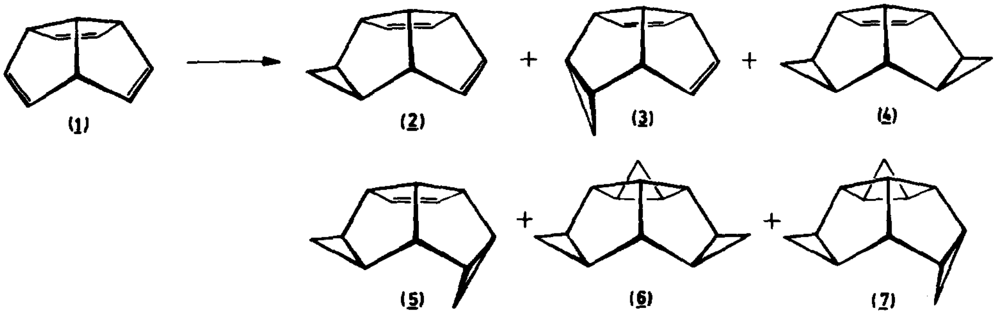
Our current interest [2] in intra- and intermolecular cycloaddition reactions of triquinacene (1) and triquinacene derivatives has lead us to study the cyclopropanation of this non-conjugated triene in some detail. We here report on our findings with two different methylenation methods and some properties of the isolated products.

The methods employed were the cuprous chloride catalyzed decomposition of diazomethane [3] and the Simmons-Smith reaction in the modification of Conia et al. [4]. The products (2) - (7) were isolated by preparative scale gas chromatography and identified by spectroscopical methods [5], the structure proof rests mainly on their ^{1}H-NMR spectra (see table 1).



With both methods the cyclopropanation of the first double bond in (1) yields both exo- (2) and endo-monohomotriquinacene (3) [6]. It is in accord with the general observation of the higher steric requirements for the latter reagent [7] that (2) predominates by a larger fraction in this case (see table 2).

Table 1: ^{1}H-NMR Data of Cyclopropanated Triquinacenes. (Chemical Shifts in τ Units)

Compound	Olefinic Protons	Bridgehead Protons	Cyclopropyl Methine Protons	Cyclopropyl Methylen Protons
(2)	4.39 (AA'BB' system, 4 H)	6.23 (m, 1H) 6.85 (m, 3H)	8.71 (dd, 2H)	9.43 (dt, 1H) 10.10 (dt, 1H)
(3)	4.58 (AA'BB' system, 4 H)	6.30 (m, 1H) 6.58 (m, 3H)	8.52 (m, 2H)	9.66 (dt, 1H) 9.90 (dt, 1H)
(4)	4.46 (s, 2H)	6.88 (d, 2H) 7.36 (dt,1H) 7.45 (d, 1H)	8.72 (m, 4H)	9.40 (dt, 2H) 10.21 (dt, 2H)
(5)	4.50 (AB system, 2H)	6.50 (dd,1H) 6.74 (dt,1H) 7.06-7.26(m,2H)	8.48 (m, 2H) 8.76 (dd,2H)	9.37-9.77(m,3H) 10.28 (dt, 1H)
(6)	-	7.47 (s, 4H)	8.59 (dd,6H)	9.45 (dt, 3H) 10.35 (dt, 3H)
(7)	-	7.16 (m, 3H) 7.72 (m, 1H)	8.44 (m, 2H) 8.68 (m, 4H)	9.07 (dt, 1H) 9.38-9.76(m,3H) 10.44 (dt, 2H)

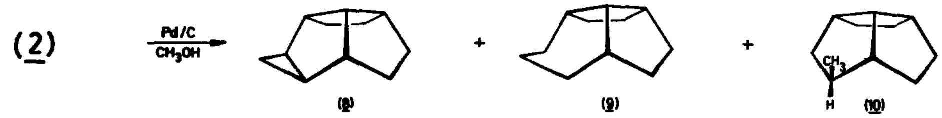
Table 2: Relative Yields of Cyclopropanated Triquinacenes (Determined by Analytical Gas Chromatography)

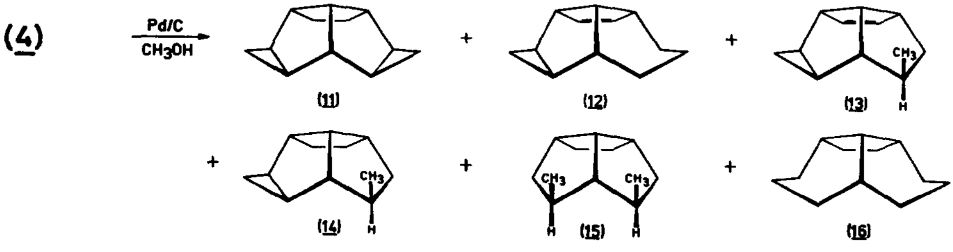
Method	Products						
	(1)[a]	(2)	(3)	(4)	(5)	(6)	(7)
Gaspar-Roth [3] 40 fold excess of reagent[b]	20%	31%	11%	18%	12%	3%	5%
Simmons-Smith [4] 3.3 fold excess of reagent[c]	4%	19%	5%	41%	4%	22%	5%

[a] Recovered starting material. [b] 10 percent pentane solution of (1).
[c] 20 percent ethereal solution of (1).

Addition of a second methylene in (2) can again occur from the exo- or endo-side to give exo,exo- or endo,exo-bishomotriquinacene [6]. However, further cyclopropanation of (3) with any method can apparently add methylene only from the *exo*-side, as there are only two isomeric bishomotriquinacenes, no *endo*,*endo*-isomer could be detected. Consequently, only two isomeric trishomotriquinacenes [6], the *all*-*exo*- (6) and the *endo*,*exo*,*exo*-isomer (7) are formed upon cyclopropanation of all three double bonds in (1). In line with the pronounced preference for *exo*-attack of the *Simmons*-*Smith* reagent (vide supra) the *exo*,*exo*- and *all*-*exo*-isomers (4) and (6) respectively were the main products when this method was employed (see table 2). In one experiment, a 10 percent pentane solution of pure (4) was subjected to the reaction with diazomethane/cuprous chloride, using a 60 fold excess of reagent, (6) and (7) were formed in 33% total yield and a ratio of 2.2:1.

The homotriquinacenes [6], especially (4) and (6), are of interest with respect to the possible homoconjugative interaction between the cyclopropyl groups. For the photoelectron spectroscopic investigation of this effect [8] the hydrogenated derivatives *exo*-tetracyclo$[5.3.1.0^{4,11}.0^{8,10}]$undecane (8) and *exo*,*exo*-pentacyclo$[6.3.1.0^{2,4}.0^{5,12}.0^{9,11}]$dodecane (11) were needed as reference compounds. Upon catalytic hydrogenation (10% Pd/C) (2) in methanolic solution readily took up 2.4 equivalents of hydrogen to yield three products:





(8) (16% rel. yield), (9) (33%) and (10) (51%) [9]. When (4) was hydrogenated with 1.8 equivalents of hydrogen under the same conditions the following products could be isolated: (11) (37%), (14) (12%), (15) (17%), (16) (31%) and two unidentified compounds (3%). However, when only 1.0 equivalent of hydrogen

was used, eight components could be detected by gaschromatography. Aside from unreacted (4) (30%) they were: (11) (27%), (12) (16%), (13) (10%), (14) (7%), (15) (4%), (16) (2%) [9] and two unidentified compounds (4%).

These observations bear some interesting features. Apparently the double bond and a cyclopropane ring in (4) are hydrogenated with comparable ease. Isolated (11) and the all-exo-trishomotriquinacene (6) took up hydrogen much more slowly than (4) under identical conditions, the main product from (11) was (15) (73% rel. yield) along with (14) (17%) and (16) (10%). It appears that the double bond in (4) facilitates the adsorption of the molecule on the catalyst's surface and that more than one hydrogen molecule can be transferred during one adsorption stage.

We are currently investigating possible photochemical and thermal rearrangements of the homotriquinacenes (2)-(7). Preliminary studies of the photochemical reactions of (2) show, that the main processes are intramolecular [2+2] cycloaddition and photoreduction [10].

References and Footnotes

[*] Adress correspondence to this author.

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[2] cf. D.Bosse and A.de Meijere, Angew.Chem. 86, 706 (1974); Angew.Chem. Internat.Ed. 13, 663 (1974)

[3] W.von E.Doering and W.R.Roth, Tetrahedron 19, 715 (1963)

[4] J.M.Denis, C.Girard and J.M.Conia, Synthesis 1972, 549

[5] Correct molecular weights as determined by mass spectrometry and/or satisfactory elemental analysis data were obtained for all new compounds.

[6] Systematic names: (2) and (3): exo- and endo-tetracyclo$[5.3.1.0^{4,11}.0^{8,10}]$undeca-2,5-diene; (4) and (5): exo,exo- and endo,exo-pentacyclo$[6.3.1.0^{2,4}.0^{5,12}.0^{9,11}]$dodec-6-ene; (6) and (7): all-exo- and endo,exo, exo-hexacyclo$[7.3.1.0^{2,4}.0^{5,13}.0^{6,8}.0^{10,12}]$tridecane

[7] cf. W.Kirmse and K.Pöhlmann Chem.Ber. 100, 3564 (1967)

[8] P.Bischof, D.Bosse, R.Gleiter and A.de Meijere, to be published.

[9] The structures of (8)-(16) were assigned on the basis of their ^{1}H-NMR spectra [5].

[10] D.Bosse and A.de Meijere, to be published.