Pergamon

Tetrahedron Letters, Vol. 35, No. 31, pp. 5619-5620, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01097-8

A Novel Type of Substituted Cyclopentadiene Dimer

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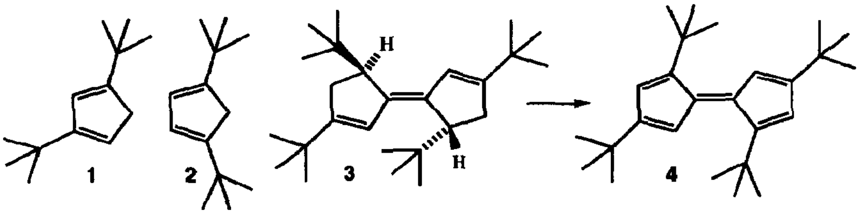
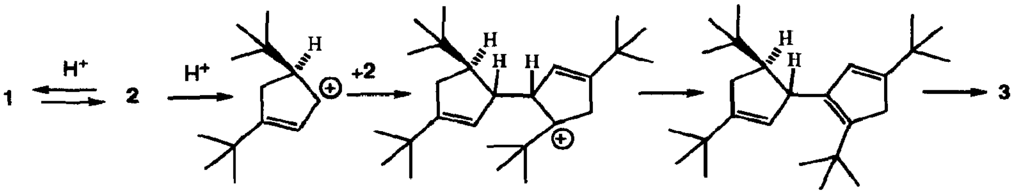
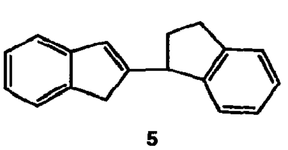
Abstract: We report here on an unusual new mode of cyclopentadiene dimerization (to give **3**) which was discovered independently by both of our groups in the course of ongoing research on reactions of highly substituted cyclopentadienes.[1,2]

A dimer $C_{26}H_{44}$ was formed as a by-product in several conversions of di-tert-butylcyclopentadiene, in the beginning under ill defined and hard-to-reproduce alkylation and cycloaddition conditions. Elaboration showed that the new compound is formed in high yield from the cyclopentadiene (equilibrium mixture of **1** and **2**, approximately 4:1) by addition of a trace of iodine or a drop of trifluoroacetic acid to the neat liquid. No such reaction occurs if iodine is given to a solution of **1/2** in an inert solvent.



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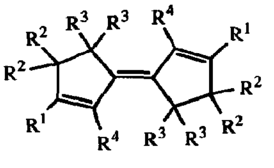

6a R^1 to R^4 = H
6b R^1, R^2 = CH_3; R^3, R^4 = H
6c R^1, R^4 = Cl; R^2, R^3 = F

Characterization by C,H analysis and spectral methods established the structure as (E,E)-3,3',5,5'-tetra-tert-butyl-4,5,4',5'-tetrahydro-1,1'-bi(cyclopentadienylidene), **3**.[3] Most revealing are an UV absorption at 296 and 308 nm (log ε 4.76 and 4.61) in ether, the presence of three olefinic signals in the ^{13}C NMR spectrum and the coupling pattern in the ^{1}H NMR spectrum.[4]

The formation of **3** in the acid catalyzed reaction can be rationalized easily as shown in the scheme. Conceivably, the iodine promoted process could be of a radical nature, but addition of various radical promotors did not have any influence. Possibly a trace of acid is formed also in the iodine reaction by iodination / dehydroiodination. - Mild oxidation [5] transforms **3** into the known [6] pentalene **4**.

Not unexpectedly, tri-tert-butylcyclopentadiene cannot be dimerized in this way, and cyclopentadiene itself is polymerized. The acid catalyzed dimerization of indene, however, has been known since 1911 [7], the dimer structure (**5**) since 1979 [8]. A search of C.A. and Beilstein-on-line data bases furnished only a few compounds related to **3**: E/Z mixtures of **6a** [9], **6b** [10], and **6c** [11]. None of these was obtained by acid (or iodine) catalyzed dimerization.- We intend to investigate the scope of this new dimerization using other pure multiply alkylated cyclopentadienes.

Acknowledgement: This research was supported, in part, by the Fonds der Chemischen Industrie. H.S. is grateful to Prof. O. J. Scherer for generous support.

References and Footnotes:

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3. Iodine Catalysis: 3.56 g (20 mmol) **1/2** are stirred with 70 mg iodine. A green color develops within a few hours. Stirring is stopped, when crystallization sets in. The mixture is kept overnight at room temperature, then treated with acetone. The product is filtered off and recrystallized from acetone. Yield 1.78 g (50 %), m.p. 166° C. - ^{1}H NMR ($CDCl_3$): δ 0.77 (s, 18 H), 1.08 (s, 18 H), 2.24 (d, 2H, J = 16.3 Hz), 2.39 (ddd, 2H, J = 13.3, 7.0, 2.1), 2.68 (d, 2H, J = 7.0), 5.89 (d, 2H, J = 2.1).- ^{13}C NMR ($CDCl_3$): δ 28.6, 29.2, 33.3, 34.6, 36.3, 52.4 (d, J = 133 Hz), 127.8 (d, J = 160), 138.5 (s), 154.1 (s). -MS : 356 (M^+).- $C_{26}H_{44}$ (356.6) Calc. C 87.56 H 12.44; found C 87.70, H 12.60.

   Acid Catalysis: 1.78 g (10 mmol) **1/2** are stirred with a drop of trifluoroacetic acid at room temperature. Precipitation of **3** begins after 2 h. After 20 h 25 ml petroleum ether (30 - 60°C) are added, the solution is washed with aq. $NaHCO_3$ and dried with Na_2SO_4. The solvent is removed and the product is crystallized from acetone. Yield: 800 mg (45 %).
4. There is an allylic coupling of J = 2.1 Hz with only one, perpendicularly oriented hydrogen atom of the CH_2 group. The same H couples to the single hydrogen at the tert-butyl carrying carbon (J ≈ 7 Hz) and to its geminal partner (J ≈ 16 Hz), whereas the other hydrogen of the methylene group gives only a doublet.
5. 2.0 g (5.6 mmol) of **3** are stirred with 3 g (13 mmol) 2,3-dichloro-5,6-dicyanoquinone in CH_2Cl_2 for 72 h. The solvent is removed, and the residue is extracted with petroleum ether 30 - 60°C). After concentration and cooling 0.79 g (40 %) of deep-red needles are obtained, m.p. 142°C (lit. m.p. 145°C [6]). The NMR spectral data are indentical to those of the known compound **4**.[6]
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(*Received in Germany* 6 *May* 1994; *accepted* 6 *June* 1994)