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REACTIONS OF DI- AND TRI-*TERT*-BUTYLCYCLOPENTADIENES WITH DIHALOCARBENES

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Abstract: *Dihalocarbene additions to mixed 1,3- and 1,4-di-tert-butylcyclopentadienes (**1**, **3**) allow to prepare 1,3-di-tert-butyl-4-halobenzenes (**9**) in an efficient way. Only the 3,4 double bond is attacked regiospecifically in 1,3,5-tri-tert-butylcyclopentadiene (**11**) (and also in **1**).Totally unexpected main products from **11** are compounds **9** again being formed under fragmentation of a tert-butyl group. Only small amounts of 1,2,4-tri-tert-butyl-5-halobenzenes (**13**, X = Cl, Br) are obtained from **11**. A labile primary dichlorocarbene adduct to **11** (**12a**) can be isolated. Its thermal decomposition occurs with the loss of one tert-butyl group to yield **9a**. Base catalyzed degradation of **12a** gives **9a** and **13a** as by-product.*

A phase transfer catalytic (PTC) method was developed recently which allows to prepare poly-tert-butylated cyclopentadienes in very high yields. [1-4] The ensuing investigation of the reactivity of these molecules showed that many "normal" chemical conversions do not preceed due to excessive shielding of the double bonds.[5] The present investigation is concerned with the following questions: (a) Do these cyclopentadienes react with dihalocarbenes, and which double bond is attacked ? (b) Is this reaction a good method to prepare certain substituted *tert*-butylbenzenes ?

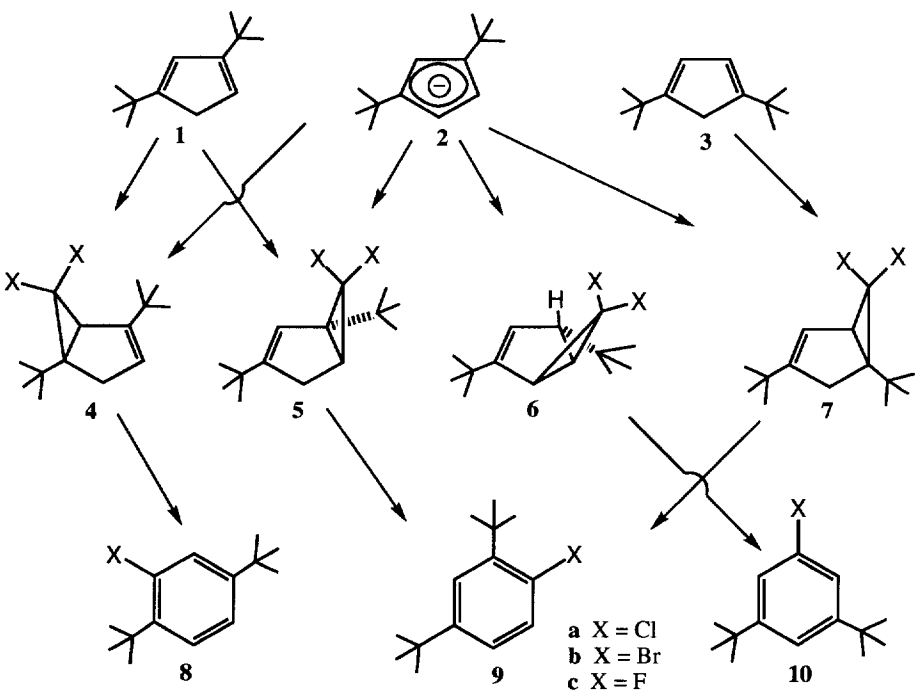
Di-*tert*-butylcyclopentadiene is formed as a 4 : 1 mixture of the 1,3- and 1,4-isomers **1** and **3**. It is well known that alkylated cyclopentadienes are less acidic than the parent compound.[6,7] Nevertheless, the formation of a small equilibrium concentration of anion **2** is sufficient to accelerate the isomerization **1** → **3**. (Scheme 1) Furthermore, **2** itself could possibly be trapped by the carbene. Thus, the outcome of the carbene addition is unpredictable *a priori* : Intermediates **4** and **5** could be formed from **1**, intermediates **4** - **7** (plus double bond isomers of **5** and **7**) from **2**, and **3** can only give intermediate **7**. Even though some simple bicyclo[3.1.0]hex-2-enes have been prepared in substance[7], such compounds are labile normally and aromatize rapidly. HX-Elimination would effect these transformations: **4** → **8**, **5** or **7** → **9**, and **6** → **10**. Other types of dichlorocarbene additions to unsubstituted cyclopendadiene have been recorded and might potentially also be possible here: 3,3,7,7-Tetrachlorotricyclo[4.1.0.0^{3,5}]heptane [8] and 6-chlorofulvene [9] were prepared under certain conditions.

For our experiments, the dihalocarbenes were generated from haloforms and concentrated sodium hydroxide in the presence of benzyltriethylammonium chloride (TEBA; PTC method). Intermediates could not be isolated, and the starting materials were used up totally at the end of the conversions. Working with dichloro-, dibromo-, and chlorofluorocarbenes, single products were formed in 78, 77 and 75% isolated yields. NMR

spectra permit the identification as 1,3-di-*tert*-butyl-4-halobenzenes (**9 a - c** ; X = Cl, Br, or F, respectively). **9a** [10], **9b** [11], and **9c** [12] have been prepared recently by much more circumstantial methods. To verify the structures,[13] **9b** was metalated with n-butyllithium and then quenched by methanol to yield 1,3-di-*tert*-butylbenzene.

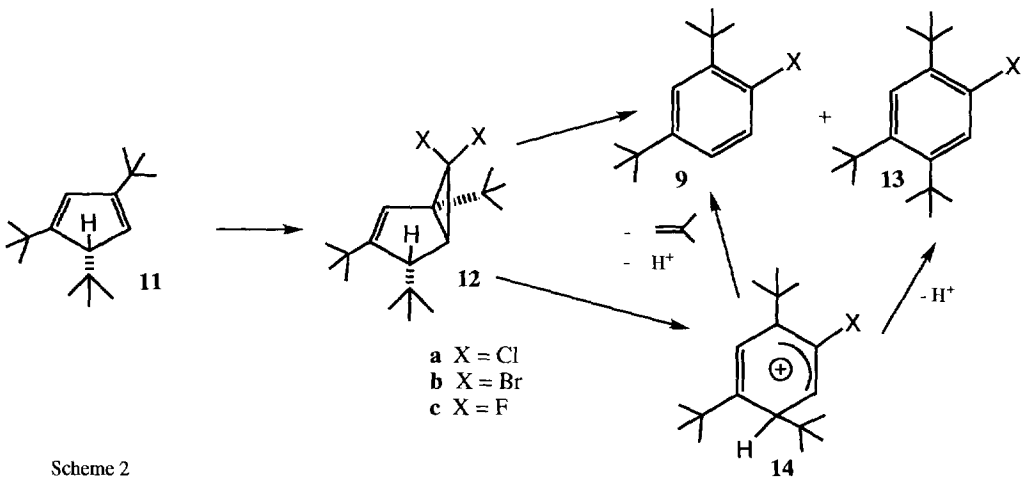
Probing for deprotonation/isomerization, the mixture of **1** and **3** in dichloromethane was stirred with a large excess of 30% $NaOD/D_2O$ in the presence of TEBA at room temperature for 1.5 hours. Only partial exchange was found, and this was somewhat more extensive in the saturated positions. This indicates that deprotonation is possible under the conditions of the PTC carbene generation. There is no fast total equilibration, however, and all three species, **1**, **2**, and **3** are candidates for carbene additions. The fact, that **9** is the sole product, does not exclude **1** as a reacting species. This becomes more apparent from the reactions of **11** (see below).

Sole formation of 1,3-di-*tert*-butyl-4-fluorobenzene (**9c**) demands intermediate(s) **5** and/or **7** with *endo*-chloro and *exo*-fluoro substituents in line with the Woodward-Hoffmann-De Puy rules. [14] *endo* Selectivity for the larger atom is not rare among the additions of carbenes carrying two different halogens. [15] Although no general theoretical explanation or calculation of this effect seems to have been performed, it is interpreted usually *via* a favorable interaction of the more polarizable halogen with alkyl substituents on the alkene.



Scheme 1

Whereas the di-*tert*-butylcyclopentadienes are obtained as a mixture of **1** and **3**, 1,3,5-tri-*tert*-butylcyclopentadiene **11** is a single isomer. Its conversion with dihalocarbenes takes an unexpected course: main products are the same di-*tert*-butylhalobenzenes **9** which are formed from **1/3**. Only small amounts (9 or 7% yields) of tri-*tert*-butylchloro- or -bromobenzenes (**13a,b**) and no respective fluoro compound were found (Scheme 2). Structures of **13a,b** rest on the presence of two aromatic singlets in the NMR spectrum establishing a *para* relation. Thus, the intermediates are **12a-c**. The exclusive carbene addition to only one of the double bonds of **11** (and **1**) is remarkable as both olefinic sites are trisubstituted and do have a similar sterical environment. There is precedence, however, that cyclopropanation of a 2-substituted 1,3-diene is (electronically) favored at the double bond carrying the branching substituent. As a matter of fact, 2,4-dimethylpentadiene gives a 88 : 12 ratio of the two possible dichlorocarbene adducts and only one dibromocarbene adduct always in preference of the less substituted, but 2-methyl carrying double bond. [16]



Scheme 2

Spectroscopic analysis of the crude reaction mixtures from **11** indicated that a low concentration of the intermediate **12a** was present in the chloro case. **12b** and **12c** were not detected in the respective mixtures. When **11** was treated with ethyl trichloroacetate / sodium methoxide at 0°C and worked up carefully, however, rather labile **12a** was obtained in a pure form. A coupling of 1.3 Hz between the ring protons in the NMR spectrum supports the expected stereochemistry (tert-*butyl* group at C-4 and cyclopropane ring *anti* as shown in Scheme 2) with an dihedral angle close to 90°.

12a is transformed into **9a** exclusively by refluxing in dichloromethane. The same product results if **12a** is treated with silver nitrate in methanol at room temperature. Finally, the reaction of the dichloromethane solution of **12a** with 50% KOH/TEBA at room temperature overnight gives a mixture of **9a**, **13a**, and unchanged **12a** in the ratio of ca. 3 : 1 : 4. Apparantly **12** is opened to give ion **14**. In the thermal and silver ion catalyzed processes, this is fragmented under loss of 2-methylpropene and a proton to give **12**. When base is present, either HX elimination from starting compound **12** or deprotonation of ion **14** compete, however inefficiently. *The spontaneous, high-yield fragmentation of a tert-butyl group in this crowded molecule is quite remarkable.*

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ with the Bruker AM 300 instrument.

Dihalocarbene additions to *tert*-butylcyclopentadienes (general procedure) : 10 mmol of **1/3** are dissolved in 5 ml of dichloromethane and 75 mmol of haloform. 0.12 mmol TEBA are added, and the mixture is stirred with 15 ml of 50% aqueous NaOH for 4 h at room temperature. The reaction mixture is diluted with 200 ml of water, the phases are separated, and the aqueous layer is extracted with dichloromethane. After drying (Na_2SO_4), the solvent is removed and the residue is distilled in a Kugelrohr. - The reaction with dichlorofluoromethane is started at -20°C and brought to room temperature gradually.- Reactions of **11** were performed on a 3-fold larger scale. Separation of compounds **9** and **13** is effected by spinning band distillation.

1,3-Di-tert-butyl-4-chlorobenzene (**9a**), b.p. 80°C /0.5 torr, yield 78 %; NMR identical to lit.[10]

1-Bromo-2,4-di-tert-butylbenzene (**9b**), b.p. 85°C /0.5 torr; lit.[11c]: 113-115 °C /2.5 Torr, yield 77%; NMR identical to lit.[10,11]

1,3-Di-tert-butyl-4-fluorobenzene (**9c**), b.p. 55°C /0.2 torr; lit. [12]:105-106°C/13 Torr. yield 75 %; ^1H NMR: δ 7.30 (dd, 1H, J=2.5 (H,H) and 5.6 Hz (H,F coupling)), 7.16 (ddd, 1H, J=2.5, 8.5 (H,H), and 4.5 (H,F), 6.87 (dd, 1H, J=8.5 and 12.4), 1.38 (s, 9H), 1.30 (s, 9H).

1,3,4-Tri-tert-butyl-5-chlorobenzene (**13a**), b.p. 110°C /0.5 torr; ^1H NMR: δ 7.61 (s, 1H), 7.49 (s, 1H), 1.53 (s, 9H), 1.52 (s, 9H), 1.46 (s, 9H). - $C_{18}H_{29}Cl$ (280.9) calc. C 76.97 H 10.41; found C 76.97 H 10.52.

1-Bromo-2,4,5-tri-tert-butylbenzene (**13b**), m.p. 77°C. - ^1H NMR: δ 7.70 (s, 1H), 7.61 (s, 1H), 1.522 (s, 9H), 1.520 (s, 9H), 1.49 (s, 9H). - $C_{18}H_{29}Br$ (325.3) calc. C 66.45 H 8.98; found C 66.25 H 9.16.

1,3,4-Tri-tert-butyl-6,6-dichlorobicyclo[3.1.0]hex-2-ene (**12**): 20 mmol **11** are dissolved in 40 ml of dichloromethane. 50 mmol of ethyl trichloroacetate and 6 g of solid sodium methoxide are added at 0°C and the mixture is stirred overnight at this temperature. The solvent is removed *in vacuo*, and the residue is extracted with ether. Careful removal of the solvent at low temperature gives a slightly yellow oil. Colourless crystals separate after prolonged standing at - 15°C. Yield 2.16 g (66%), m.p. 40°C. - ^1H NMR: δ 5.72 (t, 1H, J = 1.3 Hz), 2.66 (d, 1H,J = 1.3 Hz), 2.05 (d, 1H, J = 1.3 Hz), 1.17 (s, 9H), 1.16 (s, 9H), 1.07 (s, 9H). - $C_{18}H_{30}Cl_2$ (317.3) calc. C 68.13 H 9.53; found C 68.14 H 9.27.

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