ORIGINAL PAPER

Tetra-*tert*-butylethylene, fantasy, fake, or reality?

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Abstract This paper reviews all recent attempts to prepare tetra-*tert*-butylethylene. Some of the synthetic pathways approached this molecule very close but failed during the last step. According to recent DFT calculations this alkene should be a stable molecule with a strain energy in the range of 93 kcal/mol. Since all synthetic approaches failed new methodologies have to be developed, that is either synthesis of the perfluoro derivative of this alkene or the reaction of the radical cation or the radical anion of di-*tert*-butylmethane with the carbene by a crossed beam technique in the gas phase.

Abbreviation

(1) Tetra-*tert*-butylethylene

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(2) Di-*tert*-butyldiisopropylpropylethylene
(3) Tri-*tert*-butylethylethylene
(4) Tetraaldehyde
(5) Di-*tert*-butylcarbene
(6) *anti*-fenchylidenefenchane
(7) 1,2-Di-*tert*-butyl-3,3,5,5-tetramethylcyclopentene
(8) Tetra-*tert*-butylethane
(9) 1,1-Dimethyl-2-*tert*-butylcyclopropane

Introduction

Tetra-*tert*-butylethylene (**1**) has been the subject of a large number of synthetic attempts for chemists for more than the last three decades [1] Fig. 1. In principle, compound **1** is not a complex molecule in that it has high symmetry and no obvious "exotic" functionality. It has but three types of carbons and but one for C–H bonds. However, its synthesis has not been accomplished, because no successful synthetic entry for its preparation has been found. Time has become by now to more fully discuss and answer the question, why this molecule has not been prepared. To say it is highly strained because of its four *tert*-butyl groups is only the beginning of our discussion.

Barton and Guziec, along with their respective coworkers found already during the time between 1972 and 1976, that neither the corresponding five-membered 1,3,4-Δ^3-thia (nor selena)-diazoline could be prepared by starting from the corresponding derivatives of di-*tert*-butylketone [2], while the E/Z isomers of 1,2-di-*tert*-butyl-1,2-diisopropylethylene (**2**) has been prepared by use of the Barton-Kellogg's extrusion method [2]. Krebs and his group tried several methods, they ended in synthesis of tri-*tert*-butylethylethylene (**3**) [3]. They were also very "close" to alkene **1**, since they could prepare the tetraaldehyde (**4**), an ethylene derivative with

Fig. 1 Formula of compounds
1–9, see text.
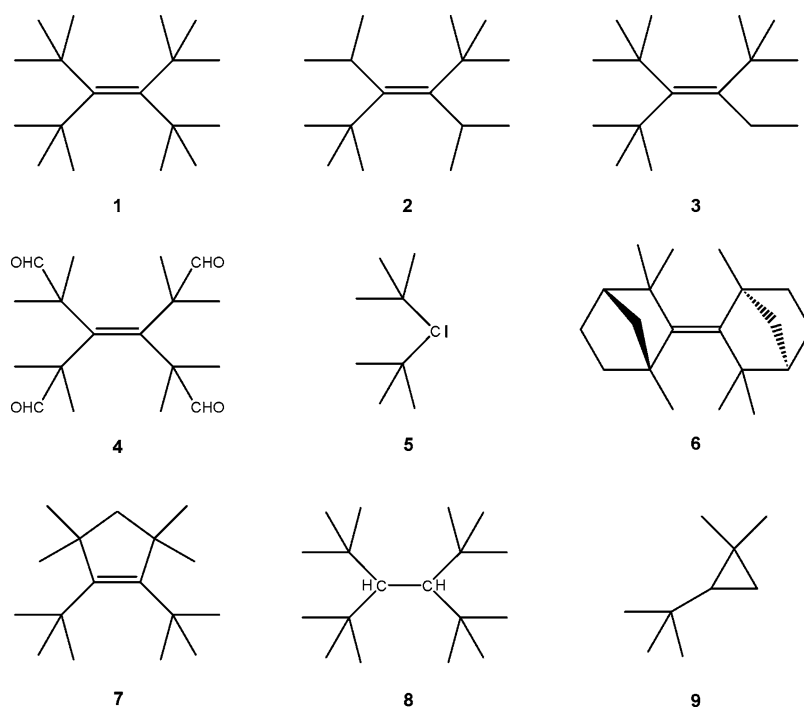
four C(CH$_3$)$_2$CHO groups affixed to the double bond [4, 5]. Unfortunately, the seemingly easy reduction of the aldehyde to methyl groups of compound **4** turned out to be a very complex matter. During reduction of aldehyde **4** with LiAlH$_4$ cyclization of a first formed CH$_2$OH group with a nonreacted aldehyde group did occur. Other reducing methods for aldehydes like Wolff-Kishner reduction were not successful–decarbonylation mostly resulted. All attempts to prepare 1,1,2-tri-*tert*-butyl-1-ethanol, a starting material for β-elimination to give alkene (**1**), failed completely due to strain of this material [6]. McMurry coupling of di-*tert*-butylketone leads only to reduction of the carbonyl to the carbinol group without a trace of any C,C coupling product [7]. Recently Ephritikine et al. found also some reduction of the keto to a methylene group, when di-*tert*-butylketone was treated with TiCl$_4$/Li [7c]; a carbenoid species was deduced as intermediate by the authors. They have been several attempts to dimerize di-*tert*-butylcarbene (**5**), but neither low temperature photolysis of di-*tert*-butyldiazomethane [8], nor thermal decomposition of di-*tert*-butyldiazomethane yielding carbene **5** on metal surfaces any dimerization products were obtained [9]. It should be mentioned that several "tied-back" derivatives of alkene 1 such as *anti*-fenchylidenefenchane (**6**), have been successfully prepared [2, 10]. However, all subsequent attempts to follow this route for synthesis of alkene **1** failed [10]. Besides of alkene **6**, a specially designed cyclic "tied-back" derivatives of alkene **1** other cyclic alkenes such as 1,2-di-*tert*-butyl-3,3,5,5-tetramethylcyclopentene (**7**) and its

higher homologue, the cyclohexene derivative, has been prepared quite recently by Nakayama et al. [11]. Alkene **7** was prepared from diethyl-2,2,4,4-tetramethylglutarate in a 14 step synthesis. The double bond is introduced via intramolecular condensation of the diazo- with selenoketone function of the carbon chain and subsequent double extrusion of the selenodiazoline [11]. While the six-membered ring alkene, the next higher homologue of alkene **7** can also be prepared, the higher homologue with a seven member ring failed in this approach, this compound with sulfur in the ring would be the direct candidate for synthesis of desired alkene **1** by hydrogenation. Several other crowded alkenes have been prepared by use of McMurry reaction from the corresponding ketones: these results are reviewed in papers [7a,b].

Only two more failures of attempted syntheses of alkene **1** should be cited here. Hydrogenation of the cyclopropyl group of tetrakis(1-methylcyclopropyl)ethylene gives the wrong isomer (an ethylmethyl group is formed instead of trimethyl, *sec*-butyl instead of *tert*-butyl) [12], reaction of tetraacetylethylene with excess dimethyltitanium chloride did not give alkene **1** but a derivative of bicyclo[3.3.0]oct-5-ene [13]. It should be mentioned that 1,1,2,2-tetra-*tert*-butylethane (**8**) has been prepared by reaction of dibromodi-*tert*-butylmethane by treatment with metals like sodium, potassium and magnesium in THF [14]. This result shows already qualitatively, that it is easier to elongate a C,C single bond than a C,C double bond, a not altogether surprising result given the characteristic ir stretching frequencies of both types of bonds.

Why does carbene 5 not dimerize?

There are recent DFT calculations on carbene **5** and its pathways to dimerize to give alkene **1**, [15] using DFT methods on BLYP/DZd level. First, di-*tert*-butylcarbene **5** has a triplet ($\sigma^1\pi^1$) ground state in agreement with experimental observations. The calculated singlet-triplet splitting is calculated to be 2.9 kcal/mol, sensibly larger than that of dimethylcarbene and smaller than the parent CH_2 itself. Dimerization of carbene **5** to yield the alkene **1** is strongly exothermic, an enthalpy value of $\Delta H = -73.7$ kcal/mol-olefin has been calculated. But carbene **5** has an alternative unimolecular reaction channel, which is kinetically favoured by both concentration and orientation effects. This is the intramolecular C–H insertion into one of the six methyl groups, to give 1,1-dimethyl-2-*tert*-butylcyclopropane (**9**). This pathway is observed experimentally and calculations give an explanation for this finding. While C–H insertion of triplet **5** to compound **9** has a low barrier of $\Delta G^{\#}$ of ca. 5 kcal/mol, while the barrier for dimerization of carbene **5** to singlet alkene **1** is calculated by $\Delta G^{\#}$ of 25 kcal/mol! The enthalpy calculated for the reaction of carbene **5** to give insertion product **9** is 87 kcal/mol-olefin, or some 44 kcal/mol-carbene, much lower than the value for dimerization.

Structural and electronic parameters calculated for alkene 1, comparison with other alkenes

The singlet-triplet split of alkene **1** is calculated (BLYP/DZd) to be 12.6 kcal/mol [15]. As shown in this computational study, besides elongation of the C,C double bond to 1.46 Å, the vinylic C,C bonds are also strongly elongated compared to normal vinylic bond length found in normal alkenes like propene. The main distortion is twisting of the double bond to an angle of 45°.

The strain energy of alkene **1** is in the range of 93 kcal/mol, DFT-calculations and molecular mechanics lead to nearly the same number for this value. Other di-*tert*-butyl-dialkylethylenes [3b] have much lower values for strain energies, they are in the range of 20–30 kcal/mol with torsion angles in the range of 15–25°. What is the general result of geometry changes in strained alkenes? The double bond becomes twisted and out-of-plane bent besides of its elongation, in addition the vinylic bonds become also longer [16]. There are specially strained alkenes, which show a pyramidalization of the double bond preferentially [17].

The most distorted alkenes (twisting at the double bond) are the following compounds: bis[1,3-bis(dicyanomethylene)indan-2-ylidene] (**10**) and perchloro-9-9′-bifluorenylidene (**11**), from refs/ [18, 19] respectively see Fig. 2, see text.
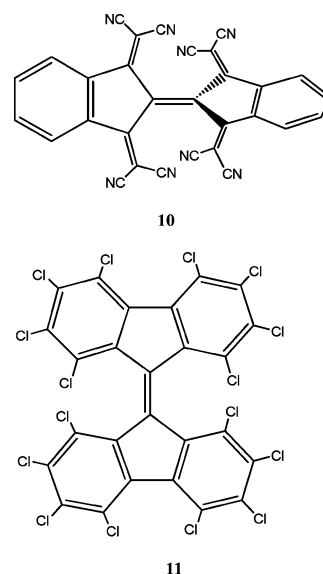
Fig. 2 Formula of most twisted alkenes, 10 and 11, see text.

According to single X-ray analysis [18] alkene **10** has a twist angle of 49°, that of **11** [19] one of 66°. It is questionable, if these alkenes have a normal "double" bond, the lengths of either bonds are intermediate between a normal single and double bond.

But it should be mentioned that there are stable organic molecules, which have a larger strain energy compared to alkene **1**. For example, although the precise value remains contentious, cubane and its derivatives have strain energies of some 150 kcal/mol, but they are generally stable, readily isolable molecules, see ref. [20].)

How might alkene 1 be prepared?

One possibility would be dimerization of the perfluoro derivative of carbene **5**. This compound is not known, but it might be prepared by "easy" synthetic routes. A closely related structure, 1,1,1,3,5,5,5-heptafluoro-2,2,4,4-tetrakis-trifluoromethylpentane has been been prepared [21]. It would be easy to oxygenate the methylene group of this compound. As precedented by the literature, e.g. refs. [22], insertion of carbenes into C–F bonds would be much more difficult to achieve. Then again, the "perfluoroalkyl effect" [23] is expected to stabilize, at least kinetically, the carbenes from subsequent reaction much as it would stabilize the perfluoroanalogue of **1** as stabilization has been seen for many other strained species such as the hexakis(trifluoromethyl)benzene valence isomers. However, this would be only the synthesis of a derivative of alkene **1.** Completely new methodologies might have to be developed. A plausible route to alkene **1** would be the reaction of the radical cation formed from (**5**) with the corresponding radical anion. They can

be formed from carbene **5** generated *in situ* from di-*tert*-butyldiazomethane by metal catalysis (e.g., electrochemically by Pt of the electrodes). The radical cation will be formed at the cathode, the radical anion at the anode. Both species will diffuse through the solution and have the chance to react with each other. In principle they could be formed electrochemically at the corresponding, but diaphragm separated, electrode from the parent diazo compound. Diffusion would allow the free radical ions to migrate in the solution and then react to form the desired olefin. There are recent reports in the literature about radical cations and radical anions of special carbenes. It may also be possible to generate the species in the gas phase and to combine them by a special cross beam technique. Finally, we note [24] when dibromodi-*tert*-butylmethane is treated with alkali metals like sodium or potassium, a complex mixture is obtained. GC/MS showed that there is a product in this mixture with the mass of 252, which might be attributed to alkene **1**.

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