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"TIED-BACK" CARBOCYCLIC INTERMEDIATES IN THE PREPARATION OF VERY STERICALLY STRAINED OLEFINS: DERIVATIVES OF TETRA-TERT-BUTYLETHYLENE

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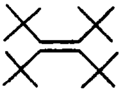
Abstract: The preparations of the extremely sterically hindered olefins (12) and (13) are described, and attempts to convert these compounds to other derivatives of tetra-*tert*-butylethylene (1) are outlined.

The preparation of very strained compounds and investigations of their chemical and spectroscopic properties continue to attract much attention.[1] Of great current interest is the chemistry of very sterically hindered olefins.[2-10] The ultimate synthetic goal in this area is the extremely hindered tetra-*tert*-butylethylene (1). Another important synthetic target is the less strained 2-di-*tert*-butylmethylenefenchane (2).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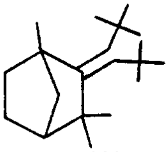
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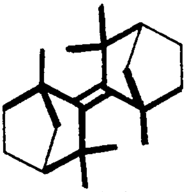
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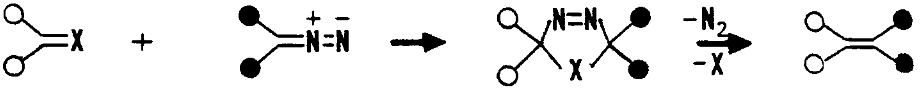
The most effective method for the preparation of very sterically hindered olefins - the twofold extrusion reaction of a selone or thione (4) with a diazo compound (5) (Scheme 1)[11] - fails in the direct attempted preparation of (1).[3,4] Apparently severe steric interactions prevent formation of the intermediate selenadiazoline (6). The ready twofold extrusion preparation of *syn*-bifenchylidene (3)[4] however, suggested a reasonable synthetic approach to tetra-*tert*-butylethylene (1). Bifenchylidene (3) can be considered a "tied-back"



(4) (5) (6)

$X = S, Se$ (Scheme 1)

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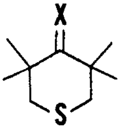
tetra-tert-butylethylene. The rigidity of the fenchane skeleton decreases steric interactions due to methyl groups in the formation and decomposition of the selenadiazoline intermediate affording (3) in good yield.

It was hoped that similar "tied-back" derivatives would prove useful in the preparation of other sterically strained olefins, and that these compounds would be convertable to (1) or (2). While the most direct approach to (1), involving the tetramethylthiacyclohexanone derivatives (7), did not lead to "tied-back" olefin (8)[8], the preparations of related compounds (9)[9] and (10)[10] led to our investigation of olefin syntheses based on the potentially functionalizable tetramethylindanone system (11).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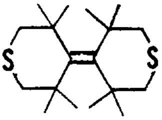
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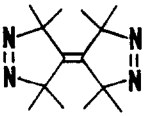
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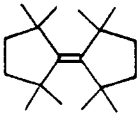
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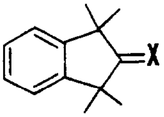
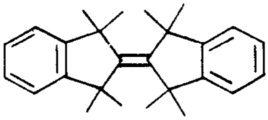

(11)

(a) X=O
(b) X=NNH$_2$
(c) X=N-NPPh$_3$
(d) X=Se
(e) X=N$_2$

The known, 1,1,3,3-tetramethyl-2-indanone (11a)[12] was converted to its hydrazone (11b), mp 106-106.5°C, in 78% yield by treatment with excess hydrazine hydrate in diethylene glycol at 160° for 48 h. Treatment of the hydrazone with triphenylphosphine dibromide - triethylamine in dry benzene afforded the triphenylphosphoranylenehydrazone (11c), mp 165°C, in 88% yield. Heating (11c) in the presence of excess selenium powder at 185°C while distilling volatiles at 1 torr into a dry ice - acetone trap, followed by a bulb to bulb distillation of the crude distillate afforded deep blue crystalline 1,1,3,3-tetramethyl-indan-2-selone (11d), mp 40-43°C, in 85% yield. Direct pyrolysis of (11c) at 185°C while distilling volatiles afforded unstable diazocompound (11e) in low yield.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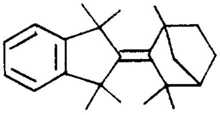
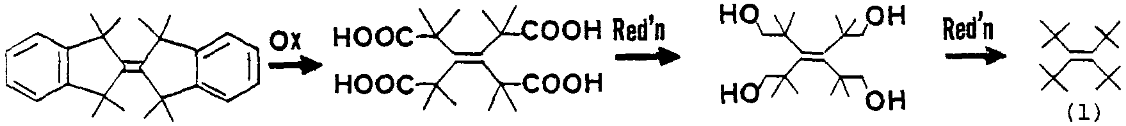

(13)

While the direct thermal reaction of selone (11d) with diazo compound (11e) afforded olefin (12) in poor yield, pyrolysis at 185°C of this selone with the phosphoranylenehydrazone (11c) under argon for 96h., and trituration of the residue with dichloromethane directly afforded colorless crystals of bi-1,1,3,3-tetramethyl-2-indanylidene (12). Recrystallization from chloroform-methanol afforded the pure olefin[13] in 65% yield, mp 255°C, NMR (CDCl$_3$) δ7.15 (br.s, 8H), 1.77 (s,24H); IR(KBr) ν_{max} 1600,1490,1450,750 cm^{-1}; m/e 344 (M+).

Conversion of (12) to tetra-tert-butylethylene (1) would require functionalization of the aromatic moiety of the olefin without concomitant reaction of the olefinic bond. It was hoped that because of the observed low reactivity of the olefinic bond in sterically strained olefins[3-5] that this transformation could be accomplished. (Scheme 2). Treatment of bi-indanylidene (12) in carbontetrachloride-water ruthenium tetroxide[14] for 8 days at 60°C quantitatively cleaved the olefinic bond.[15] No carboxylic acid derivatives could be detected in the reaction mixture. Olefin (12) is inert to bromine in carbontetrachloride, singlet oxygen, and a variety of dissolving metal reducing conditions; attempted nitration of (12) under forcing conditions led to a complex mixture of ketonic products.



(12)

(1)

(Scheme 2)

The unsymmetrical olefin , 2-(1,1,3,3-tetramethyl-2-indanylidene)-fenchane (13) could be prepared by heating a mixture of the phosphoranyl hydrazone (11c) with a 1.5-fold excess of (-) selenofenchone[4] at 195°C for 42h with stirring under nitrogen. The crude reaction mixture containing (13) (12) and (3)[16] in a ratio of 5:3:2 was triturated with cyclohexane and the soluble material fractionated using flash chromatography[17] (silica-cyclohexane). Recrystallization from chloroform-methanol afforded the crystalline olefin (13) in 20% yield, mp 103°C, NMR ($CDCl_3$) δ7.10 (br.s,4H), 2.1-0.9 (complex, 30H); IR ($CHCl_3$) ν_{max} 1600, 1490, 1365, 1030 cm^{-1}; m/e 308 (m+), 293 ($m-CH_3$).

Attempted oxidation of (13) with ruthenium tetroxide led only to cleavage of the olefinic bond affording (-) fenchone and the starting indanone (11a)

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16. Products (12) and (3) are formed due to a cycloreversion of the intermediate selenadiazoline and symmetrical recombination of reactive fragments. Similar cycloreversions have been noted in the attempted preparations of other very sterically hindered olefins.[3,4,6,8]
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