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1,4-DI-tert-BUTYLMETHYLENECYCLOPROPENE

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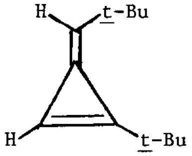
Summary: The synthesis, trapping, and spectral characterization of 1,4-di-tert-butylmethylenecyclopropene are described.

The stabilization of transient species using sterically protecting tert-butyl groups (the corset effect) is well documented[1] and finds elegant application in the synthesis of stable cyclobutadiene and tetradrane derivatives by Maier and his co-workers.[2] We wish to report some results concerning the synthesis and characterization of 1, a stable (-30°) derivative of the remaining C_4H_4 of theoretical interest, methylenecyclopropene.[3]



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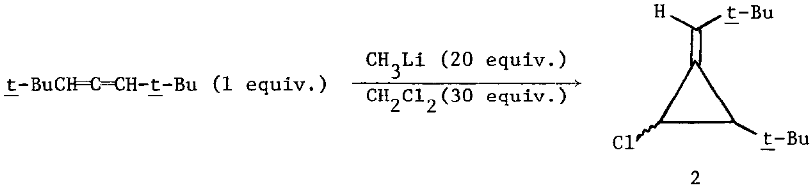
The starting material 2 (trans/cis = 55/45) was prepared in 42% yield from 1,3-di-tert-butylallene[4] and chlorocarbene (CH_2Cl_2, CH_3Li).[5] The two remaining isomers of 2, compounds



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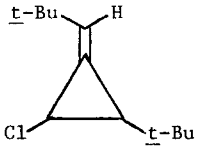
3 and 4, would arise by addition of the carbene to the hindered face of the allene and were not



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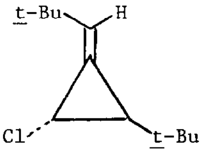

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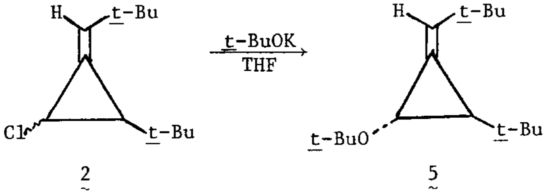
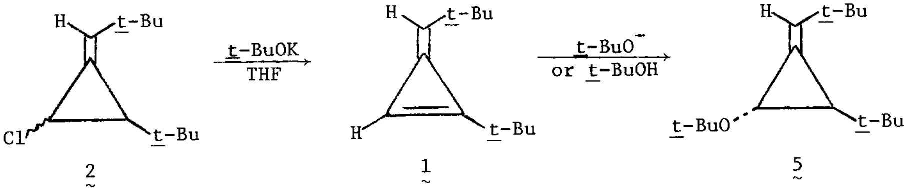
formed. The isomers of 2 gave the following spectral data: NMR (CDCl$_3$) *cis*: δ 1.11 (9 H, s), 1.13 (9 H, s), 1.83 (1 H, d of d, J = 8.2 Hz, 2.2 Hz), 3.40 (1 H, d of d, J = 8.2 Hz, 1.4 Hz) and 6.17 (1 H, d of d, J = 2.2 Hz, 1.4 Hz); *trans*: 0.96 (9 H, s), 1.12 (9 H, s), 1.78 (1 H, t, J = 2.6 Hz), 3.18 (1 H, d of d, J = 3.1 Hz, 1.3 Hz), and 6.23 (1 H, d of d, J = 2.6 Hz, 1.3 Hz); mass spectrum calcd for C$_{12}$H$_{21}$Cl 200.1332, found 200.1332.

The reaction of either the *cis* or *trans* isomer of 2 with potassium *tert*-butoxide in tetrahydrofuran at 25°C gave 5. Compound 5 was characterized by its NMR spectrum which shows three



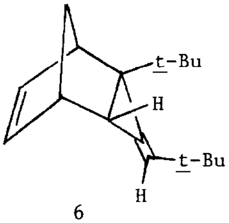
singlets (9 H each) at δ 0.95, 1.11 and 1.25 with other signals at 1.53 (1 H, t, J = 2.6 Hz), 3.21 (1 H, d of d, J = 3.1 Hz, 1.3 Hz) and 6.03 (1 H, d of d, J = 2.6 Hz, 1.3 Hz); mass spectrum calcd for C$_{12}$H$_{22}$O (M$^+$−C$_4$H$_8$) 182.1671, found 182.1670. The small coupling constant for the vicinal cyclopropyl hydrogens allows the assignment of stereochemistry as *trans*.[6]

The formation of 5 is rationalized in terms of 1 as a reactive intermediate. Stereospecific syn addition of *tert*-butoxide or *tert*-butanol would yield *trans*-5. Another interpre-



tation, *e.g.*, S$_N$2 displacement on 2, can then be discounted since *trans*-2 would give only the *cis* isomer of 5.

When 2 is reacted with potassium tert-butoxide in tetrahydrofuran at -40°C to -30°C and the volatile materials are then removed in vacuo to a second cold (liq N_2) reaction vessel containing cyclopentadiene, compound 6 is formed in 10% yield. Compound 6 exhibits NMR signals



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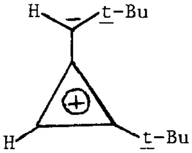
at δ 0.98 (9 H, s), 1.00 (9 H, s), 1.48-1.76 (3 H, m), 2.80 ~ 3.00 (2 H, m), 5.31 (1 H, d, J = 0.8 Hz) and 5.72-6.07 (2 H, m); mass spectrum calcd for $C_{17}H_{26}$ 230.2034, found 230.2031. The trans isomer of 2 was recovered unchanged from this experiment.

The hydrocarbon itself was characterized by NMR spectroscopy in the following way: 100 mg of cis-2 in 0.2 ml of tetrahydrofuran-d_8 was added dropwise to a solution of potassium tert-butoxide (180 mg) in 0.8 ml of tetrahydrofuran-d_8 at -60°C. After 5 hours at -40°C to -30°C the volatile materials were removed in vacuo to a second flask, transferred to an NMR tube and sealed. The NMR spectrum (-30°C) exhibits the following signals: δ 1.12 (9 H, s), 1.32 (9 H, s), 4.02 (1 H, d, J = 3.2 Hz), 7.90 (1 H, d, J = 3.2 Hz). A particularly interesting feature of the NMR spectrum of 1 is the chemical shifts of the olefinic protons which appear at δ 4.02 (exocyclic) and 7.90 (ring), emphasizing the sizeable contribution of 1a to the resonance hybrid.



1a

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