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SMALL-RING CYCLIC CUMULENES: SYNTHESIS OF A KINETICALLY STABLE EIGHT MEMBERED RING ALLENE

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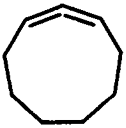
Abstract: *1-tert-Butyl-1,2-cyclooctadiene is prepared in four steps from cycloheptanone, and is found to be stable to dimerization.*

Our studies on allene photochemistry[1] have led us to examine the electronic structure and limiting ring size in strained cyclic allenes[2] and butatrienes.[3] We report here the synthesis of the first kinetically stable 1,2-cyclooctadiene.

The kinetic stability of cyclic allenes decreases rapidly with diminishing ring size.[4] 1,2-Cyclononadiene (1) is a distillable liquid,[5] while the next lower homolog 1,2-cyclooctadiene (2) can be observed by ^{1}H NMR at -60°C, but dimerizes (Scheme I) at ambient temperature.[6] There is convincing evidence for the existence and chirality of 3 and 4;[7] allene 4 has been trapped in a cryogenic matrix.[8] Among other cyclic cumulenes, known limitations for isolability include an eight membered ring ketenimine[9] and carbodiimide,[10] and 1,2,3-cyclononatriene.[3] Kinetic instability of small-ring allenes may be ascribed to strain relief, which is afforded by dimerization through C2-C2 bonding.[4b,11] This dimerization should be sensitive to steric hindrance, a technique commonly used to stabilize reactive molecules.[4]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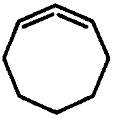
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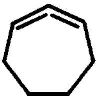
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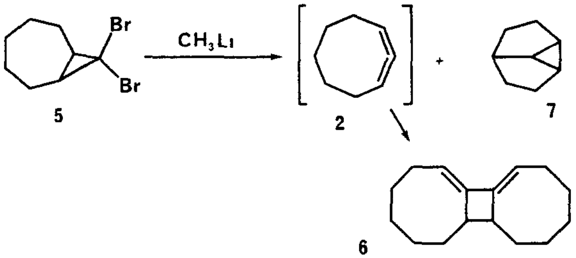
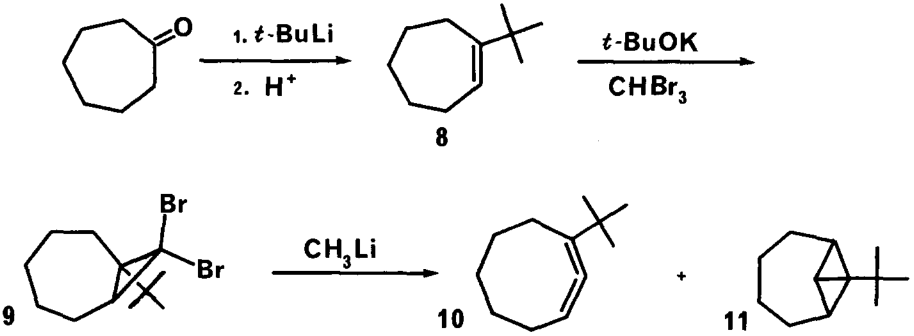
Scheme I



1-tert-Butyl-1,2-cyclooctadiene (10) was synthesized according to the straightforward route shown in Scheme II. Addition of dibromocarbene to t-butyl-cycloheptene[12] gave an 18% yield of 9.[13] Subsequent treatment with 1.1 equivalents of methyllithium in pentane at 0° afforded a 91% yield of a mixture comprised of allene 10, bicyclobutane 11, and two unidentified components (ratio 85:12:2:1 by GLC). Remarkably, both 10 and 11 proved isolable by vacuum distillation, followed by preparative GLC on glass columns.[14] Characterization of 10 as an allene follows from its IR and ^{13}C and ^{1}H NMR data.[15] The structure of bicyclobutane 11 is assigned based upon ^{13}C and ^{1}H NMR data.[16] This type of carbenoid insertion product is well precedented.

Scheme II



In contrast to the parent structure 2,[6] allene 10 did not dimerize, even on prolonged standing at ambient temperature. Hydrogenation of 10 led smoothly to t-butylcyclooctene, identical to an authentic sample, while brief treatment with p-toluenesulfonic acid or t-BuOK/DMSO gave dienes 13 and 14.[17] Acid catalyzed rearrangement undoubtedly is facilitated by relief of strain. Under identical conditions, 1 did not react, while its 1-methyl derivative rearranged very slowly.

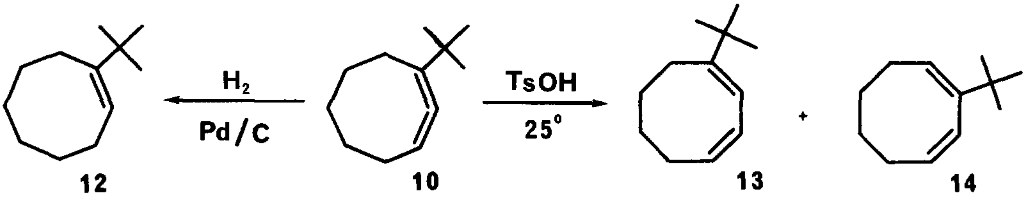
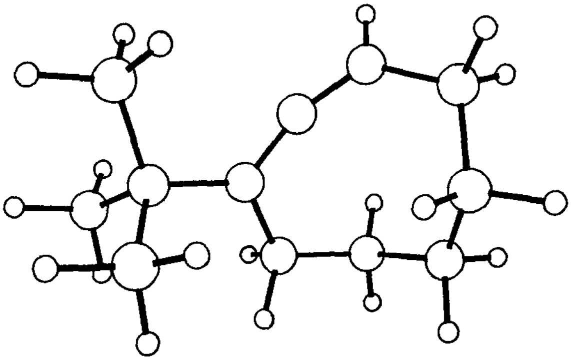


Figure 1 shows the MNDO[18] optimized structure (ΔH_f = 24.6 kcal/mol) for 10, plotted in the C1-C2-C3 plane. The allenic unit is predicted to be bent 22°, a value nearly identical to that predicted by MNDO[2] or force-field[19] calculations on the parent allene. Thus, while the allenyl moiety in 10 clearly is bent and strained, its reactivity towards dimerization is diminished due to the bulky tert-butyl group. Reactions with acid and base are enhanced.

Figure 1



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(13) Compound 9: ^{13}C NMR ($CDCl_3$) δ 52.0, 42.2, 36.8, 36.7, 34.2, 32.5, 31.2, 29.4, 29.3, 28.3; 300 MHz ^{1}H NMR δ 2.34-2.47 (m, 1H), 2.22-2.34 (m, 1HO, 1.90 (t, J=8.5 Hz, 1H), 1.61-1.90 (m, 6H), 1.33-1.51 (m, 1H), 1.27 (t, J=12.5 Hz, 1H), 1.20 (s, 9H) HR-MS calcd m/e 323.9912, obsd. 323.9917.

(14) 5'x1/8" 20% Carbowax 20M on Chromosorb W at 90°C. This strained allene is very sensitive to traces of acid on the column, and separation only worked with freshly packed columns.

(15) 1-tert-butyl-1,2-cyclooctadiene (10): 300 MHz ^{1}H NMR ($CDCl_3$) 5.30-5.22 (m, 1H), 2.25-2.12 (m, 2H), 2.00-1.77 (m, 2H), 1.66-1.30 (m, 6H), 1.07 (s, 9H); ^{13}C NMR 202.2, 117.7, 94.4 J(^{13}C - ^{1}H) = 166 Hz, 33.2, 29.3 (double width) 28.8, 28.2, 27.6, 27.2; IR (neat) 1942 cm^{-1}; HR-MS calcd m/e 164.1565, obsd. 164.1565.

(16) 1-tert-butyl-tricyclo[5.1.0.0^{2,8}]octane (11): ^{1}H NMR ($CDCl_3$) 2.66-2.61 (m, 2H), 1.73-1.66 (br s, 4H), 1.31 (pentet, J=2.9 Hz, 4H), 1.04 (t, J=3.4 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR 49.0, 33.4, 32.0, 29.4, 29.1, 27.3, 14.6; HR-MS calcd m/e 164.1565, obsd. 164.1568.

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